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# OIL & GAS JOURNAL

## Refining & Petrochemical Technology

## 1987 Edition

# Refining & Petrochemical Technology Yearbook

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# Foreword

Since 1980, the oil industry's refining and petrochemical segments have weathered low to negative margins, new governmental regulations, decreasing product demand, and excess capacity. But 1986 may have been the turning point where the downstream segment began to see improved conditions that will last into the next century.

Oil companies worldwide in 1986 saw a downstream shift in profitability from the upstream exploration, drilling, and production segments. This shift in profitability was due in part to the precipitous tumble in crude oil prices. But a great deal of the shift was the result of tightening of downstream operations since 1980 by using new and modern processing technology.

Examples of this technology are compiled in the 1987 *Refining and Petrochemical Technology Yearbook*. The examples illustrate some of the advanced concepts employed to keep the downstream segment a viable enterprise, able to supply the needs of an energy dependent world.

Poor margins during the first half of the 1980s caused many inefficient, and some efficient, facilities to be shut down. Shedding of excess capacity meant that remaining capacity could be run at higher utilization rates thus improving profitability of those operations. But capacity utilization increases alone weren't the only reason for an improved downstream picture. Technology improvements played a vital role in boosting the efficiency of the remaining operations.

Technology helped reduce energy requirements to produce a given amount of finished product. It helped improve product specifications so that the producer could maximize product value. And it helped reduce maintenance downtime and turnarounds to maximize use of the process equipment.

In the U.S., advances in technology helped the industry meet tougher governmental regulations. Worldwide, increased environmental concerns are also being met with improved technology.

In refining, the U.S. industry appears to have finally achieved an approximate balance between capacity and demand. Yearly drops in refining capacity since 1980 have appeared to cease. Preliminary figures for 1986 show that capacity will be about the same as 1985, and, due to increases in demand spurred by low crude oil prices, capacity may increase a bit through 1995. In fact, demand increases have caused gasoline production to be driven to close to maximum capability.

But achieving this better health cost the industry dearly during the 1980s. Since 1980, U.S. refining capacity fell from about 18.5 MMb/d to a current 15.4 MMb/d. This plunge in capacity resulted in the closure of 114 of the 303 refineries in operation in 1980.

Some of the decline was the shut down of inefficient operations that sprang up from the entitlements program of the 1970s. These never were viable operations and probably should never have been built. But part of decline was closure of efficient operations that got caught up in the slide. This was particularly tough on the industry because the U.S. has always lead the world in refining technology, unlike some of the "smokestack" industries that had difficulty maintaining the technological pace of the rest of the world.

By 1985, the capacity plunge began to subside and a capacity-demand balance began to appear. But the Environmental Protection Agency (EPA) delayed the return to health by mandating the elimination of lead antiknock compounds from gasoline.

This meant the industry would have to meet gasoline octane requirements via processing rather than by additives. Some of the octane could be produced by running existing processes harder, but a substantial portion would have to be produced through the use of better technology.

Better technology emerged during 1985 to cope with the EPA requirements. The fluid catalytic cracking process, responsible for about 40% of U.S. gasoline production, saw the introduction of special catalysts that boosted the octane of the gasoline product from the unit. These catalysts required special chemical technological developments that include improved zeolite composition and special catalyst matrix arrangements to maximize gasoline octane while minimizing volume yield reduction.

The isomerization process showed rapid growth during 1985 and 1986. This process basically converts the low-octane, straight-chain $C_5/C_6$ naphtha molecules to branched molecules of higher octane. The beauty of this technology is that it can be accomplished by modifying idle catalytic reformers to isomerization at a relatively low investment cost. Some 150,000 b/d of new isomerization capacity has been added since 1984.

Process improvements now allow refiners worldwide to produce a valuable product slate from a wide variety of both high- and low-quality crude oils. A refiner now has the ability to take advantage of favorable feed costs and still produce a quality product slate, for the most part, regardless of feed quality.

Heavy, high-sulfur crudes can be handled as a matter of course because of developments in heavy oil processing and sulfur removal processes. These processes can make quality products from poor-quality feeds while minimizing environmental pollution. Heavy oil processing technology will grow in importance as crude supplies decrease in quality and environmental concerns grow.

As developing nations grow, energy demands shift from fuel for heat and light to transportation fuels. This means that refineries in these areas of the world will be investing in modern technology to meet an increasing demand for gasoline, diesel, and jet fuel.

A major element of advanced processing technolgy is the incorporation of advanced catalysts that are the key to many of the modern gasoline and heavy oil processing operations. Developments are occurring rapidly and refiners now have a wide variety of catalyst choices available. During the past two years, more than 300 new catalysts became available to improve the operation of almost all of the various refining processes. And new catalyst formulations now in the developmental stage promise even greater processing capability.

Petrochemical producers have also enjoyed some profitability during the last two years. Many expect profitability to continue because of lower feedstock costs associated with the low crude oil prices of recent months and because plants are utilizing modern technology to improve plant efficiency.

Although there is still excess capacity worldwide for many major products, some are reaching the upper limits of the installed capacity to produce them and will be in short supply soon, if they aren't already. Even where current concern is for overcapacity, which now exists for ethylene, the size of the world petrochemical market could make short work of the excesses. Some say that even at a modest 3%/year growth in demand, the excess may disappear by 1990, requiring new ethylene capacity to be onstream by then.

Basic petrochemicals such as ethylene are a commodity. This means that in order to be profitable in the market, a producer has to be a low-cost producer. As a result, the petrochemical industry is launching more projects aimed at increasing its ability to make the best use of the most cost-effective feedstocks and technology.

By some estimates, an average of about 70% of petrochemical investment will be directed toward cost reduction and modernization. In some instances, plant modernization and energy improvements will account for up to 90% of investment.

Recent new ethylene plants reflect this investment strategy. Where previous plants were designed for ethane feedstock, a primary ethylene plant feed, the new plants are designed to feed it plus various liquid feedstocks such as naphtha and atmospheric and vacuum gas oils. In this present period of low priced crude oil, liquid feeds cost less, making them more attractive than ethane.

To allow the use of the liquid feeds, new cracking furnace technology that shortens the reaction time in the furnace is being utilized in new plants that prevents cracking of the feed into undesirable byproducts. New burner technology is also required to adequately handle a wide variety of fuels for ethylene furnaces.

Refiners and petrochemical producers are putting computers, micros, minis, and mainframes, to use in ever increasing numbers to tighten product specifications, closely track plant economics, and control processes at optimum conditions.

Plants use computers to quickly digest feed and product data so that feed and product slates can now be changed in as little as a week. This allows fast response to feed and product price volatility to maintain optimum profitability. Advanced computer process control concepts are also being utilized to not only produce a higher quality product, but also to produce the product at optimum economic conditions.

Refineries and petrochemical plants consume a large amount of energy in their operations, most of it consumed as steam and electricity. The passage of the Public Utilities Regulatory Policies Act (PURPA) in 1978, allowed plants to pursue a new avenue to reduced energy costs by utilizing an old technology called cogeneration. Cogeneration simply produces steam and electricity at the same time more efficiently than producing either alone. The PURPA regulations enhance the value of cogeneration by requiring a public utility to purchase excess electricity generated by a private cogenerator.

As a result, many plants have recently installed cogeneration facilities, some producing as much as 1,000 megawatts of power, that have substantially reduced power cost. One Gulf Coast plant reports its power cost has been lowered from about 5¢/kwh of electricity to about 1.5¢/kwh. Cogeneration has experienced rapid growth in the process industry during the last five years, and it is expected that substantial investment in cogeneration facilities will continue into the next century.

The examples of modern technolgy contained in the *Yearbook* range from complete processes to basic analytical techniques. It is hoped that a representative sample is given, reflecting technologies used in most of the common processing operations.

It is also hoped that the information in the articles will be directly useful to plants worldwide. But if not directly useful, the articles will serve as a foundation to spur the imaginations of process engineers throughout the industry to develop even better processing technology.

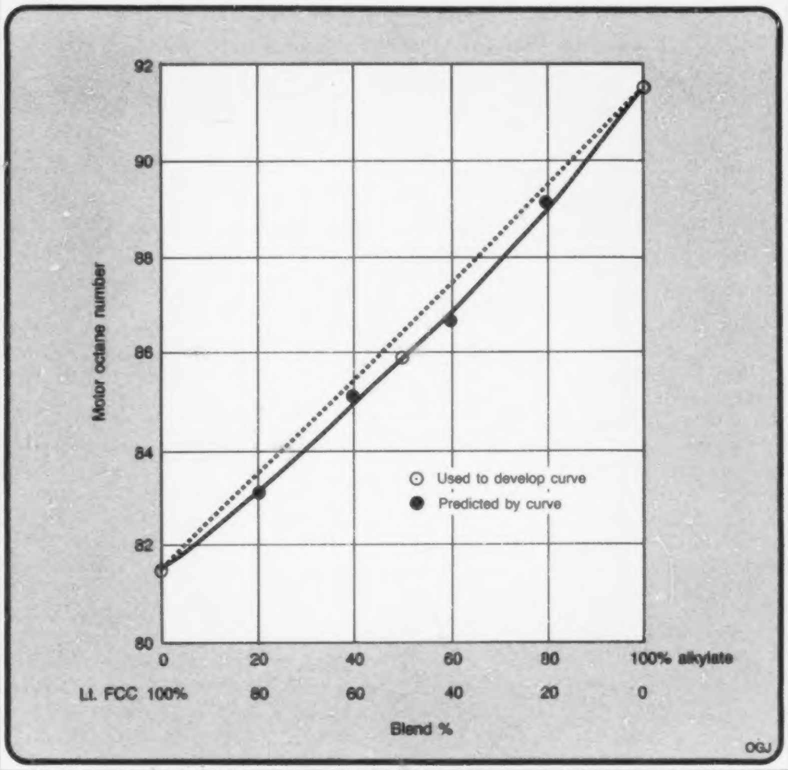
Richard A. Corbett
Refining/Petrochemical Editor
*Oil & Gas Journal*

# Optimum blending gives best pool octane

**William E. Morris**
William E. Morris Inc.
Wilmington, Del.

Fig. 1

Interaction blending of lt. FCC gasoline, alkylate



Optimum blending of gasoline components can increase the pool octane by 0.1 to 0.5 numbers. To achieve the optimum octane blending scheme, accurate octane blending values must be obtained.

These blending values can be developed from an interaction blending study or from generalized predicted interaction coefficients.

Many refiners are blending in a non-optimum fashion so that there are some cheap octanes available for the taking by simply changing to an optimum blending scheme. A study of 1984 gasoline compositions indicated that many refiners were blending in a non-optimum fashion and that "pool octane" could have been increased almost 0.5 octane.[1]

The term pool octane usually refers to the weighted average octane of all of the gasoline components. It can be calculated by multiplying the octane of each component by its fraction of the pool and adding the results.

If the components are blended into two or more grades, a second pool octane could be calculated by multiplying the octane of each grade, before any lead antiknock addition, by its fraction of the total pool. The second pool octane will differ from the first because the components do not blend linearly. The octane of a 50:50 blend of two components may be higher or lower than the average of the octanes of the two components.

With a given set of components, specifications for two or more grades of gasoline can be met with many different blending schemes. In each case the pool octane will be slightly different. The optimum blending scheme will give the highest pool octane.

How can a refiner be assured that the cheap octanes available through optimum blending are in fact being obtained? There are three essential requirements:

1. The refiner must have accurate information on how components blend together.
2. That information must be used along with specifications and other constraints in linear programming optimization to develop optimum blending compositions.
3. Blending must be done in accordance with the linear programming results.

Over the years, many octane blending studies have been carried out at individual refineries to develop blending equations for a specific set of components. Results of those studies have helped refiners make closer approaches to optimum blending.

The most modern scheme for octane blending studies is to test individual components and 50:50 blends (interaction blending approach).[2] Results facilitate calculation of interaction coefficients which describe the non-linearity of octane blending.

For unleaded blends of two components, the interaction blending equation is as follows:

$$\text{Octane no.} = a_1x_1 + a_2x_2 + b_{1,2}x_1x_2$$

where:

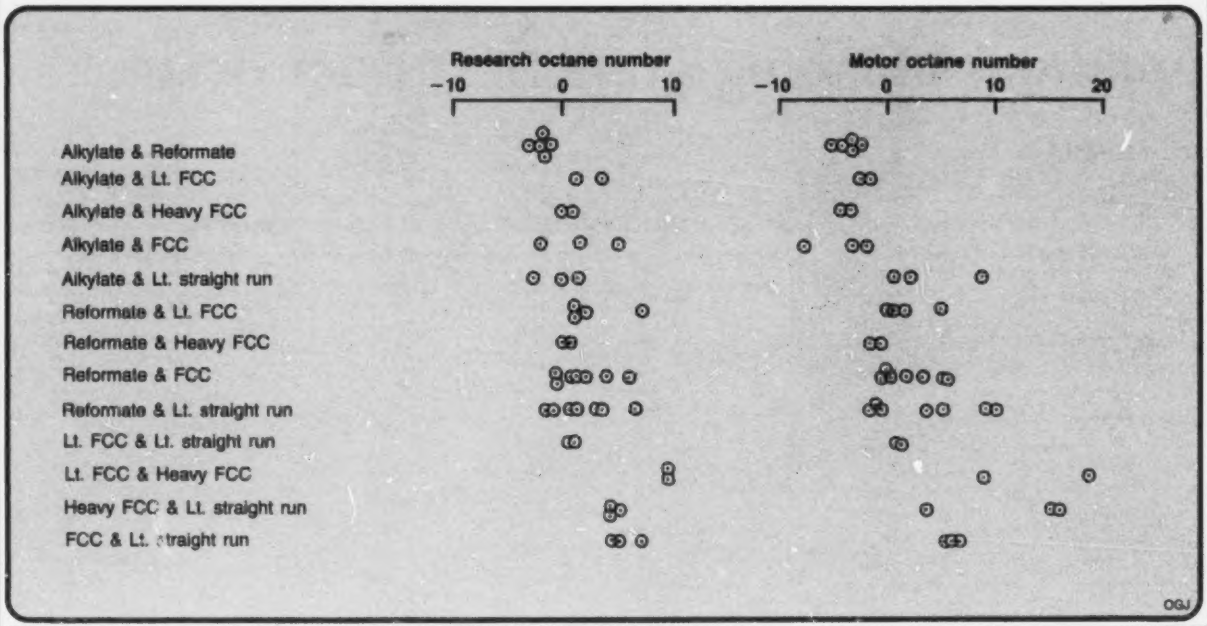
$a_1$ = Octane no. of Component 1
$a_2$ = Octane no. of Component 2
$x_1$ = Volume fraction of Component 1
$x_2$ = Volume fraction of Component 2
$b_{1,2}$ = Interaction coefficient for Components 1 and 2

The equation for leaded blends is more complex.[2]

To illustrate the use of the equation, motor octane number (MON) data for blends of light fluid catalytic cracked (FCC) gasoline and alkylate are shown in Fig. 1. The 50:50 blend is 0.6

Fig. 2

Unleaded interaction coefficients



octane below the average. The equation is:

$$MON = 81.5x_1 + 91.5x_2 - 2.4x_1x_2$$

For the 50:50 blend, the interaction term is $(-2.4)(0.5)(0.5)$ or $-0.6$. The equation was used to develop the curve in Fig. 1. The curve predicts the four check points well within experimental error.

For three or more components, there is an additional linear term for each component, and an interaction term for each pair of components. An interaction equation to describe the unleaded blending behavior of five components will have 5 linear terms and 10 interaction terms. Experience has shown that interaction equations predict octane number accurately for any multicomponent blend.

The key to accurate octane blending equations is accurate interaction coefficients. They can be developed with an octane blending study wherein accurate octane data are obtained on all components and all 50:50 blends.

Disadvantages of such studies are that they are expensive and time consuming. Over a period of time they may become outdated if significant changes occur in the gasoline pool, such as addition of new components or large changes in reforming severity.

The ideal solution is to have an accurate generalized method to predict interaction coefficients without the need for a blending study. Such a method is commercially available but is not in the public domain.

However, a limited amount of octane data is available in the literature which permits calculation of reasonably accurate interaction coefficients.[2] [3] [4] Those data have been analyzed for this article. Only unleaded interaction coefficients have been calculated, but leaded data are available in these references and others.[5] [6]

A total of 45 interaction coefficients were calculated for six major gasoline components. Detailed results are given in Table 1 and illustrated in Fig. 2.

Interaction coefficients are consistently negative for alkylate with reformate, and consistently positive for FCC gasoline with light straight run. The component-oriented interaction approach facilitates development of generalized blending equations because the non-linearity of blending is divided into many parts which can be handled separately.

For some pairs of components, an average interaction coefficient will suffice. For others, simple correlations can be developed with the component octane data. Specifying component type and octane level is equivalent to specifying hydrocarbon composition within fairly narrow limits.

Alkylate and light straight runs are both 100% saturates, but average motor octane interaction coefficients with FCC gasoline are $-4$ for alkylate and $+6$ for light straight run. Raffinate, a lower octane saturate component, had a $+20$ interaction coefficient with FCC gasoline based on data for a single blend.[2]

This effect of octane level, and of any other variables that cause such differences in interaction coefficients, is handled simply by considering alkylate, light straight run, and raffinate interactions separately. Octane level effects can, of course, be considered within each component type.

Reformates have a wide range of octane levels, and interaction coefficients change considerably with octane level. Publications do not include enough data over a sufficiently

Table 1

## Component octanes and interaction coefficients (I)

| COMPONENT TYPES 1 | 2 | Reference | RESEARCH 1 | RESEARCH 2 | RESEARCH I | MOTOR 1 | MOTOR 2 | MOTOR I |
|---|---|---|---|---|---|---|---|---|
| ALKYLATE | & REFORMATE | 2, Table A | 94.9 | 91.0 | −2.0 | 91.5 | 82.8 | −2.8 |
| | | 2, Table B | 90.5 | 85.8 | −2.4 | 89.4 | 78.0 | −3.2 |
| | | 2, Table B | 90.5 | 92.9 | −1.6 | 89.4 | 82.6 | −4.8 |
| | | 3* | 94.5 | 91.3 | −1.6 | 91.8 | 82.3 | −3.2 |
| | | 4, Table 3 | 94.0 | 83.2 | −2.0 | 92.8 | 78.0 | −0.9 |
| ALKYLATE | & LT. FCC | 2, Table A | 94.9 | 92.3 | 3.6 | 91.5 | 81.5 | −2.4 |
| | | 3* | 94.5 | 85.5 | 1.2 | 91.8 | 77.4 | −1.6 |
| ALKYLATE | & HVY. FCC | 2, Table A | 94.9 | 88.3 | 0 | 91.5 | 78.6 | −4.0 |
| | | 3* | 94.5 | 82.0 | 0.8 | 91.8 | 76.0 | −3.6 |
| ALKYLATE | & FULL-BOILING FCC | 2, Table A | 94.9 | 90.4 | 1.6 | 91.5 | 80.3 | −3.2 |
| | | 2, Table B | 90.5 | 90.4 | 4.8 | 89.4 | 78.7 | −2.0 |
| | | 4, Table 3 | 94.0 | 89.1 | −0.5 | 92.8 | 79.6 | −7.9 |
| ALKYLATE | & LT. STRAIGHT RUN | 2, Table A | 94.9 | 66.4 | −2.8 | 91.5 | 66.4 | 0.8 |
| | | 2, Table B | 90.5 | 75.6 | 1.2 | 89.4 | 74.7 | 2.0 |
| | | 3* | 94.5 | 63.2 | 0 | 91.8 | 58.7 | 8.8 |
| REFORMATE | & LT. FCC | 2, Table A | 91.0 | 92.3 | 0.8 | 82.8 | 81.5 | 0.8 |
| | | 3* | 91.3 | 85.5 | 0.8 | 82.3 | 77.4 | 0 |
| | | 4, Table 5 | 85.4 | 91.8 | 7.0 | 78.6 | 79.9 | 4.9 |
| | | 4, Table 7 | 98.6 | 94.4 | 1.0 | 86.3 | 80.1 | 0.2 |
| REFORMATE | & HVY. FCC | 2, Table A | 91.0 | 88.3 | 0.8 | 82.8 | 78.6 | −0.8 |
| | | 3* | 91.3 | 82.0 | 0 | 82.3 | 76.0 | −1.6 |
| REFORMATE | & FULL-BOILING FCC | 2, Table A | 91.0 | 90.4 | 0.4 | 82.8 | 80.3 | 0 |
| | | 2, Table B | 85.8 | 90.4 | 2.0 | 78.0 | 78.7 | 5.2 |
| | | 2, Table B | 92.9 | 90.4 | −0.8 | 82.6 | 78.7 | 1.6 |
| | | 4, Table 2 | 97.5 | 90.8 | −0.8 | 85.8 | 79.4 | −0.4 |
| | | 4, Table 2 | 90.3 | 90.8 | 1.6 | 81.3 | 79.4 | 3.2 |
| | | 4, Table 20 | 90.2 | 94.1 | 3.5 | 81.4 | 79.8 | 0 |
| | | 4, Table 22 | 81.5 | 92.6 | 5.9 | 74.8 | 80.0 | 5.9 |
| REFORMATE | & LT. STRAIGHT RUN | 2, Table A | 91.0 | 66.4 | 0.4 | 82.8 | 66.4 | −0.4 |
| | | 2, Table B | 85.8 | 75.6 | −2.0 | 78.0 | 74.7 | −1.6 |
| | | 2, Table B | 92.9 | 75.6 | −1.6 | 82.6 | 74.7 | −0.8 |
| | | 3* | 91.3 | 63.2 | 3.2 | 82.3 | 58.7 | 9.2 |
| | | 4, Table 8 | 90.8 | 60.0 | 0.5 | 80.0 | 57.9 | 3.7 |
| | | 4, Table 9 | 96.2 | 65.7 | 2.7 | 85.3 | 63.5 | 5.3 |
| | | 4, Table 22 | 81.5 | 60.9 | 6.4 | 74.8 | 58.3 | 10.1 |
| LT. FCC | & HVY. FCC | 2, Table A | 92.3 | 88.3 | 0.4 | 81.5 | 78.6 | 0.8 |
| | | 3* | 85.5 | 82.0 | 0.8 | 77.4 | 76.0 | 1.2 |
| LT. FCC | & LT. STRAIGHT RUN | 2, Table A | 92.3 | 66.4 | 9.6 | 81.5 | 66.4 | 8.8 |
| | | 3* | 85.5 | 62.3 | 9.6 | 77.4 | 58.7 | 18.4 |
| HVY. FCC | & LT. STRAIGHT RUN | 2. Table A | 88.3 | 66.4 | 4.8 | 78.6 | 66.4 | 3.6 |
| | | 3* | 82.0 | 63.2 | 4.4 | 76.0 | 58.7 | 16.0 |
| | | 4, Table 4 | 87.2 | 66.1 | 4.4 | 77.7 | 64.0 | 15.1 |
| FULL-BOILING FCC | & LT. STRAIGHT RUN | 2, Table A | 90.4 | 66.4 | 6.8 | 80.3 | 66.4 | 6.0 |
| | | 2, Table B | 90.4 | 75.6 | 4.8 | 78.7 | 74.7 | 5.6 |
| | | 4, Table 8 | 87.6 | 60.0 | 4.3 | 77.2 | 57.9 | 5.9 |

* Reference 3, Appendix 2, Table 7

Table 2

## Gasoline component types

1. Alkylate
2. Light reformate
3. Heavy reformate
4. Full-boiling reformate
5. Light FCC gasoline
6. Heavy FCC gasoline
7. Full-boiling FCC gasoline
8. Light straight run
9. Polymer gasoline
10. Isoparaffins (isopentane, light hydrocracked)
11. Raffinate
12. Methyl tertiary butyl ether (MTBE)
13. Ethanol
14. Tertiary butyl alcohol (TBA)
15. Butane

wide range of octanes to present such effects in this article. Unpublished data include interactions with full-boiling and heavy reformates well over 100 research octane number.

Oxygenates interact quite differently with different types of gasoline components. For both methyl tertiary butyl ether (MTBE) and tertiary butyl alcohol (TBA), interaction coefficients covered a range of about 30 units in one study.[3] Because of the scarcity of published data on blends of oxygenates with gasoline components, interaction coefficients for oxygenates are not included in this article.

Refiners who use interaction blending equations can use the interaction coefficients in this article to supplment interaction coefficients developed from data on blends of their own components.

Data on 50:50 blends are preferable for developing interaction coefficients.

Accurate data on binary blends containing at least 20% of the lower volume component are acceptable. Regression ("least squares") analysis of data on multicomponent blends is not recommended, because interaction coefficients developed from such data can be very misleading.

The amount of information required for a generalized prediction of interaction coefficients depends upon the number of components a refiner has or wants to consider using in the gasoline pool. A commercially available program divides components into 15 types as listed in Table 2.

A very large test program would be required to test all the pairs of components and to test the different combinations that would be needed for each pair. For example, interaction coefficients should be developed for combinations of reformates of different octane levels with light straight runs of different octane levels. Such a comprehensive program would probably be considered prohibitively expensive for almost all refiners.

In this discusson of generalized prediction of octane interaction coefficients, it is important to remember that the goal is to obtain the cheap octanes available though optimum blending. The first requirement is to have accurate information on how components blend together.

That information can be developed from results of a blending study of the components at the refinery. The interaction approach is recommended by applied statisticians.[7] (For refiners using any other form of equation, interaction equations can be used to develop coefficients for those forms of equations.)

If the operation of the refinery is stable, the results will apply for a long period of time. If the gasoline components are expected to change appreciably within a short period of time, the refiner can expect the interaction coefficients to change. In that event, the refiner may want to consider obtaining a generalized blending program.

Using new blending equations may result in a significant change in the blending scheme obtained from a linear programming study. How can the refiner determine whether the new blending scheme provides cheap octanes?

The expected effect is quite small so a very carefully administered program is required. Here is a suggested approach. First, weigh out two sets of components in their production proportions. For each set, blend the lower volume grade or grades in their sales proportions. Combine the remainder to blend the highest volume grade. Make direct match octane comparisons between the two schemes for each grade, with many repeats for accuracy. Combine the octane differences in sales proportions

## The author...

Morris

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to obtain the difference in pool octane.

Experience indicates that at any given time, most refineries are using inaccurate octane blending values. When inaccurate blending values are used in planning the blending scheme, it is likely that the blending scheme is not optimum and that at least a 0.1 pool octane increase can be obtained with the same components by going to optimum blending. This cheap octane improvement is worth about a $1 million/year for a refiner making 100,000 b/d gasoline. Assuming a cost of 30¢/octane barrel via reforming severity:

$$(0.1\text{ octane})\ \frac{(\$0.30)}{\text{Octane bbl}}$$

$$\frac{(100{,}000\text{ bbl})}{\text{Day}}\ \frac{(365\text{ days})}{\text{Year}}$$

$$=\frac{\$1{,}095{,}000}{\text{Year}}$$

Gasoline pool octane can be maximized by utilizing accurate octane blending values that are developed from an interaction octane blending study or from generalized predicted interaction coefficients.

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# Economic modeling:

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Economic modeling is a powerful decision-support tool used to maximize the profitability of gas gathering and processing facilities.

Gas gathering and processing facilities are very complex, in terms of both operations and economics. In the early 1980s, Phillips Petroleum Co.'s gas and gas liquids group recognized a need to have more information readily available.

Many detailed reports had been prepared which included historic production levels, incomes, expenses, financial rates of return, and other information. However, there were no consistent, plant-by-plant forecasts of what could be expected to happen in the future.

In addition, natural gas liquid (NGL) prices were falling, and natural gas deregulation was anticipated. It became apparent that a quick and accurate method of evaluating trends under rapidly changing conditions and markets was essential.

Work began in earnest in May 1983. Late that year, the initial versions of economic models on 39 of Phillips' gathering and processing facilities were complete.

The models are updated annually and have evolved into an extremely useful tool that more than fulfills the original intent of providing information and identifying trends. They also have been used to optimize the facilities' operations, analyze potential changes of gas purchase and sales contracts, and to perform a great number of other analyses.

Economic models are management tools used to analyze and maximize the profitability of existing NGL extraction plants and raw gas gathering systems. By combining a material and energy balance with a financial evaluation program, the existing operating and economic performance of a facility can be determined. Coupled with anticipated changes in the gathering systems, the result is an overall picture of a facility's performance over time.

Table 1

## Economic model format

- Material and energy balance
  - Raw gas volume
  - Raw gas usage and losses
  - Plant inlet volume
    - NGL and other plant production
    - Extraction shrinkage
    - Plant fuel
    - Other uses
  - Residue available for sale
- Prices
  - NGL netback values
  - Other product netback values
  - Residue gas sales
  - Gas purchase cost
- Income and expenses
  - Gas sales income
  - NGL income
  - Other income
  - Gross income
    - Gas cost
  - Gross margin
    - Plant and system operating costs
    - Miscellaneous direct expenses
  - Ibirt
- Financial analysis
  - Indirects
  - Depreciation and tax credits
  - Income taxes
  - Net income
  - Cash generated
  - Cash flow
- Economics
  - Investments
  - Reserves acquired
  - Capital cost of connecting reserves

Taken a step further, by preparing plant and system models with consistent formats and premises, a comprehensive program can provide the anticipated profitability of the entire business line.

**Model format.** All plant and system economic models have an identical format (Table 1). There are five main sections: material and energy balance, prices, income and expenses, financial analyses, and economics.

The material and energy balance begins with raw gas volumes metered at the wellhead from which all raw gas uses and losses are subtracted to arrive at the plant inlet volume. NGL, sulfur, and other plant production are calculated, as well as plant fuel and extraction shrinkage.

The resultant residue gas volume is divided into residue sold and amount returned for field use. These balances are performed on both a volumetric basis as well as a calorific basis.

The pricing section consists of input values that result from an evaluation

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Based on a presentation made to the Rocky Mountain Regional meeting of the Gas Processors Association, Denver, Colo., Sept. 26, 1985.

# A valuable tool in gas processing

Table 2

## Typical information*

**Page 1**

| | |
|---|---|
| Plant type | Cryogenic expander |
| Capacity, MMcfd | 75 |
| Throughput, MMcfd | 69 (1984 avg.) |
| Product disposition | |
| NGL | Sold to local refiners |
| Residue | Sold to Interstate Pipeline Company (IPC) |

Gas purchase contracts:

- 24% of total raw gas purchased is under flat rate contracts ranging from 90% to 100% of residue price received.
- 66% of total raw gas is purchased under various casinghead contracts that provide for 75% of attributable residue plus about 60% of liquid value to be returned to the producer.
- 10% of total raw gas is covered by a processing agreement with IPC.

Total gross investment, $50,000,000
Tax depreciation, $31,105,977
Financial depreciation, $31,213,933

| **Current year** | **1985** |
|---|---|
| Production | |
| Average system throughput, Mcfd | 84,000 |
| Average plant throughput, Mcfd | 74,760 |
| Average residue volume, Mcfd | 58,737 |
| Average NGL production, b/d | 9,630 |
| gal/day | 404,452 |
| Financial | |
| Gross margin, $/raw Mcf | 0.92 |
| Ibirt, $/raw Mcf | 0.58 |
| Economic | |
| Total cash generated, $1,000 | 12,380 |
| Investment, $1,000 | 2,700 |
| Cash flow, $1,000 | 9,680 |
| Incremental economics | |
| AARR, % | 88.3 |
| NTEB, times | 3.0 |
| Payout, years | 2.0 |

**Page 2**

Major premises:

- Booster fuel and raw uses equal 9%, based on an in-depth study of the gathering system completed 1/1/85.
- Processed gas cost is 100% of gas price (@1,100 BTU/cf) on system inlet gas volume.
- New connection gas prices are based on current gas purchase contracts and historic gas price trends. All new contracts for high and low pressure gas use the new contract format to avoid initially unprofitable gas costs.
- Residue gas price based on the new agreement with IPC made in February 1985.
- Product prices based on a current netback at plant fence. Projections for this model are escalated at 7%/year.
- Expenses escalated at 5%/year for demonstration purposes.

Conclusions:

- The average return on assets for the future shows the plant as a strong revenue producing asset.
- Maintaining low gas cost is the key to GPA plant profitability.
- Declining liquids values are the primary reason for gross margin and Ibirt lower than last year.
- Fuel conditioners installed on the raw booster fuel optimize profitability by increasing compressor efficiency and conserving liquids.

Recommendations:

1. Continue the effort to lower gas cost by using the new gas purchase contract.
2. Continue the effort to identify and reduce raw gas uses and unaccountables.
3. Place a high priority on controlling and lowering fixed expenses.
4. Complete the study of fuel conditioners on compressors in the gathering system.

*The information contained in this model is completely fictitious and in no way is meant to represent any forecast of future prices or costs.

of the disposition of plant products, gas purchase contracts, and gas sales contracts.

The income and expenses section includes estimates of income derived from the sale of residue gas, NGL, and other plant production, and any other income derived from plant and gathering system operations. Gas cost is the first expense calculated to arrive at a gross margin, or, put another way, gross profit before operating and capital expenses.

Operating costs for both the plant and gathering system are included with general expense items, miscellaneous direct expenses, and taxes other than income tax. These are subtracted to arrive at the income before indirects, reserves, and taxes (Ibirt).

The financial section contains the indirect overhead charges, depreciation and tax calculations necessary to arrive at net income, cash generated, and cash flow. Net income is calculated by subtracting indirect charges, depreciation, and taxes paid from the Ibirt.

Cash generated is calculated by subtracting indirects and taxes from the Ibirt. Cash flow is simply cash generated minus investments.

The economics section contains anticipated future investments broken down into three separate categories: maintenance capital, plant modifications and/or expansions, and well connection investments.

The well connection costs are separated from maintenance and plant costs so that, in combination with the amount of new gas reserves acquired, the average capital cost to connect reserves may be calculated. This provides useful insights into the gathering system's maturity and can help project future capital requirements.

**Program structure.** The total gas volume of a facility is divided into three main sections: historic production, existing connected reserves, and future connected reserves. When added together, they provide the total reserves production (Fig. 1).

The historic production section covers past production and financial performance.

The existing connected reserves portion of the model forecasts future gas production from only those wells already connected to the plant's gathering system by the end of the preceding year. Operating factors for field fuel and losses, NGL retentions, plant fuel, and extraction shrinkage from the historic production section are used as constants in this existing connected reserves section, unless there are known anomalies or errors.

Production from wells being connected in the current year and in the future are included in a separate part of the model, entitled future connected reserves. Operating factors from the historic production section are used to predict the operating performance of the gathering system and plant.

The historic production/existing connected reserves portion of the model is added to the future connected reserves to arrive at total reserves production. This is the overall operating and financial performance of the facility since it includes the past production as well as estimates of future growth.

This structure has been selected for a number of reasons. First, it provides a simple way of analyzing the incremental profitability of a facility. By separating the production from existing connected reserves from future connections, the position inherent in a facility may be examined versus current and future activity.

Often, facilities that have marginal overall economics may have extremely high rates of return on incremental investments. On the other hand, other facilities are only profitable due to their position and large amount of old, cheap gas reserves, while current well connections are only marginally profitable.

By dividing the total gas stream into two parts, these differences become quickly apparent.

Fig. 1

Gas production

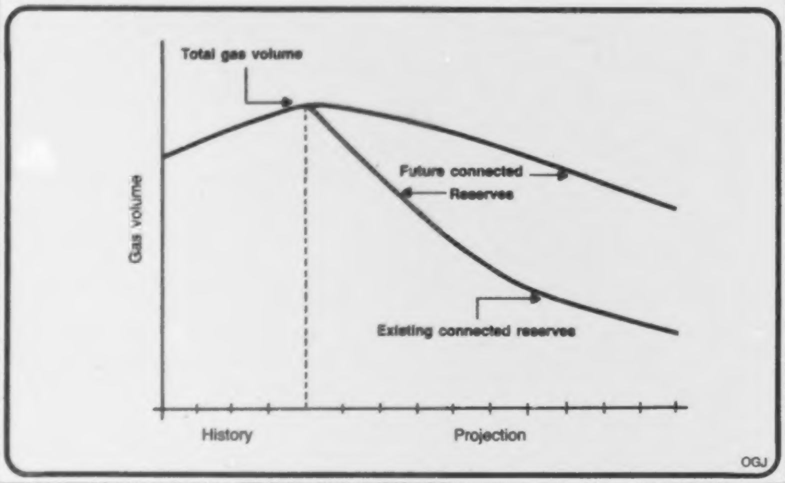


Fig. 2

Profitability analysis

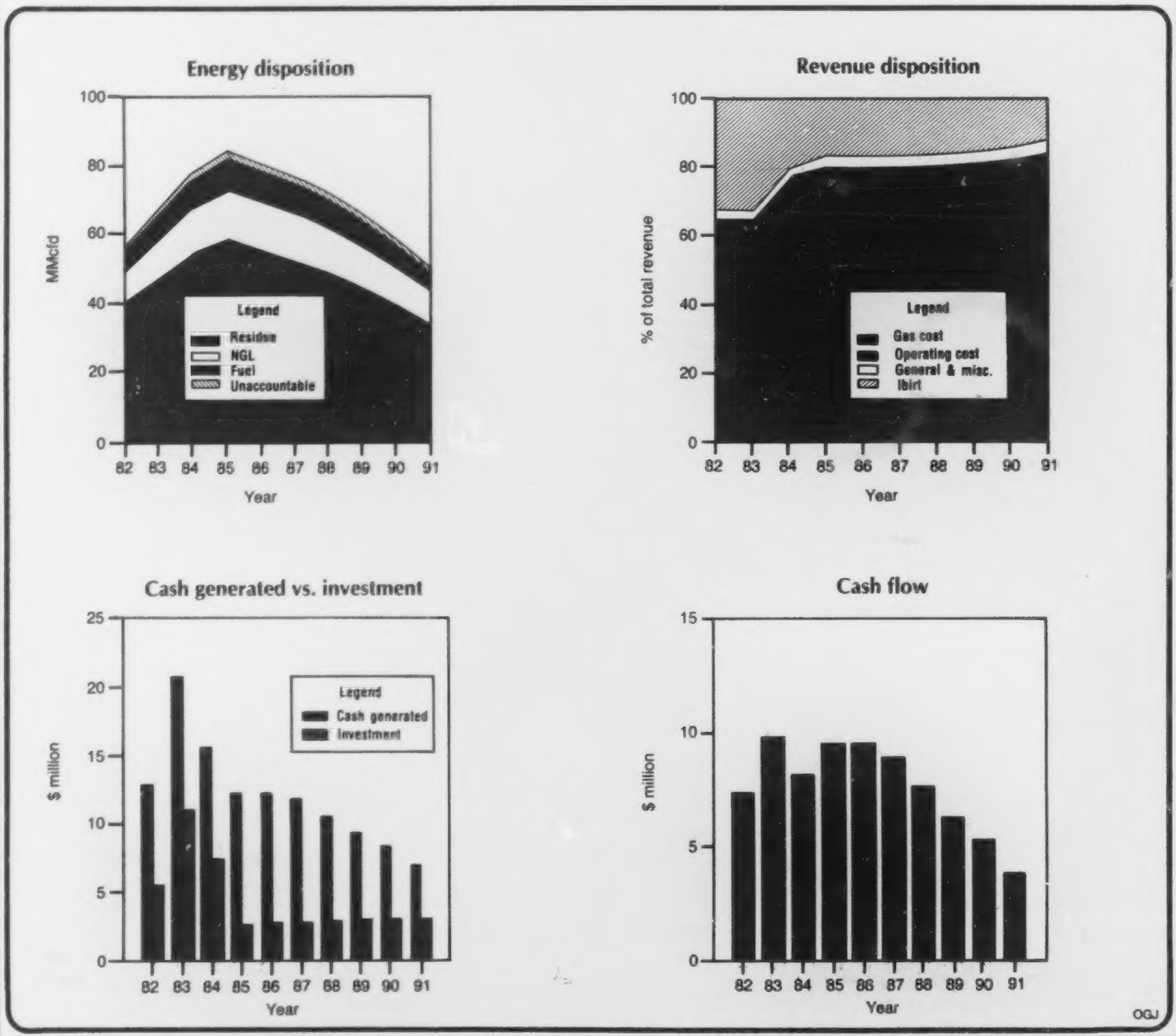
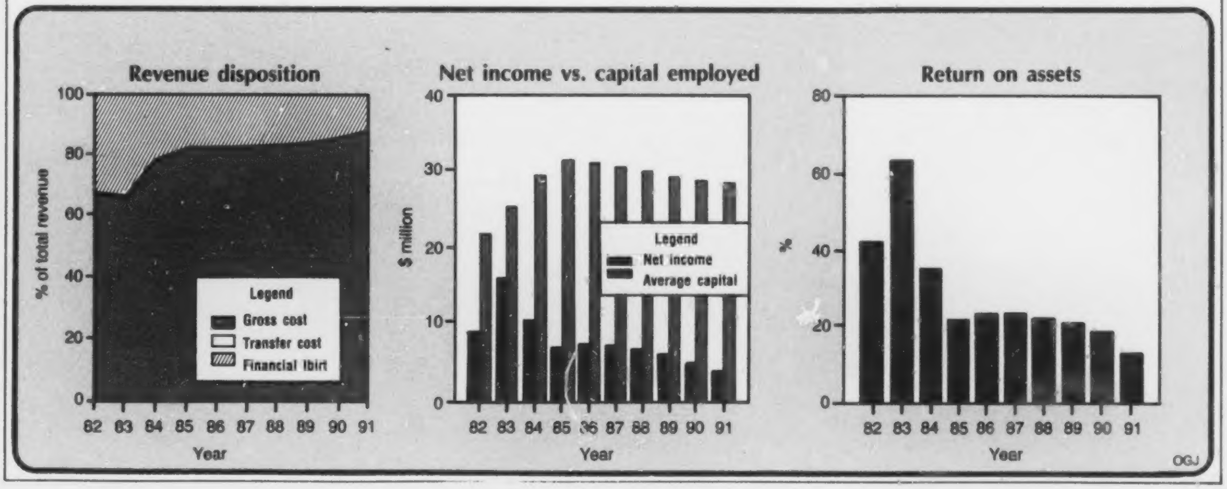


Fig. 3

## Financial analysis



Second, since each plant is being examined individually, gathering system and plant operations may be much more accurately predicted than if a regional or company-wide "macro" approach is used. This is also true of estimating future gas purchase and sales values, NGL netbacks, and operating costs.

Third, accuracy in forecasting available gas volumes can be improved since the wells already connected to a gathering system may be examined closely and projections made on the future deliverabilities. Forecasts of future well connection activity are improved since different production patterns from new fields and formations can be taken into account.

**Preparation.** The intent in preparing economic models is not to provide a super-accurate accounting document. Rather, emphasis is placed on basic premises and accurate analyses of contractual arrangements, operating conditions, expenses, future growth potential, and detailed evaluation of results.

Overall direction is the desired result, not minute detail. Minor discrepancies or errors in any one section will not negate the value of the economic model. To the contrary, by indicating where potential problem areas exist, the models accomplish the goal of providing direction for further evaluations.

In preparing the historical production section, however, attention to details is essential. Accounting records must be continually examined and large errors corrected before preparation of the rest of the model can be pursued. However, as soon as enough data are collected to be reasonably sure the overall result is correct, investigations should cease.

The material and energy balance can be prepared in several ways, depending on the records available and their accuracy. At Phillips, we have chosen to begin at the tailgate of the plant, with residue gas and NGL production, and at the wellhead, with raw gas volumes, and work towards filling in the intermediate information.

The plant products which are sold are combined on a molar basis to arrive at a plant inlet composition. Plant inlet volume is calculated by combining, also on a molar basis, plant fuel, losses, water vapor equivalent, etc., with the residue gas and NGL.

Wellhead raw gas volumes are taken from the accounting records, with its composition assumed to be equal to the plant inlet composition. Invariably, adjustments are required due to metering differences and unaccountables. These are put into the raw gas uses section of the material balance.

An alternative for preparing the material and energy balance is to begin with wellhead volumes and compositions and work forward through the gathering system and plant to the ultimate disposition of plant products. Significant errors can result, however, if these results are not closely compared to actual products sold, and adjustments made if necessary.

Product prices are readily available from accounting records, and are used on a plant netback basis. This is the actual net value derived from the sale of products after the cost of transportation and fractionation.

The analysis of gas purchase and sales contracts can be quite complex or very simple depending on the size, number, and types of contracts. This area is probably the most crucial part of the entire program, since even a small error in the basic premises of these calculations can cause a wide distortion in the facility's perceived profitability.

The income and expenses section begins with the calculation of revenues derived from the sale of residue gas and plant products. Production figures from the material and energy balance section are multiplied by the values from the pricing section to arrive at the gross income of a facility.

Official company income statements are used primarily as a check on these calculations, and significant errors investigated. Often, large discrepancies result from prior year adjustments or errors which distort the figures.

The first expense to be calculated is gas cost, which is subtracted from gross income to arrive at the gross margin. If this is too small, contractual changes are indicated, since the margin is actually the gross profit before operating costs and taxes are deducted. Optimization efforts aimed at improving profitability are futile if the contractual arrangements are unfavorable and are left unchanged.

**Fixed and variables.** Operating expenses are broken down into fixed costs and variable costs. This is done in order to provide more-accurate predictions of expenses by separating the volume-dependent charges from the volume-independent costs.

Expenses in both categories are escalated with inflation factors. However, fixed costs are not adjusted for throughput, and these charges steadily increase even if volumes decline.

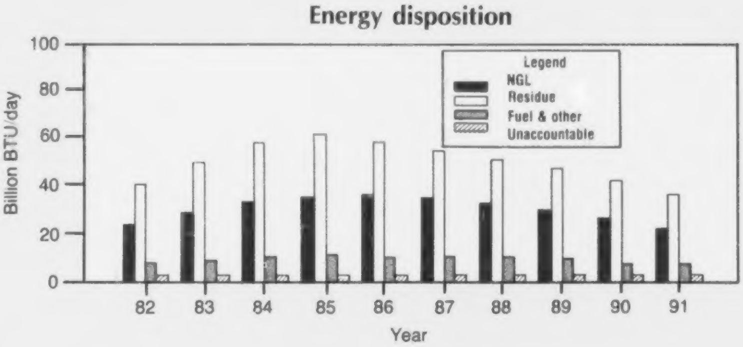
Variable costs, on the other hand, are calculated from the historic records on a unit ($/Mcf) basis and then escalated for inflation. These adjusted cost figures are then multiplied by

Fig. 4

# Operations analysis

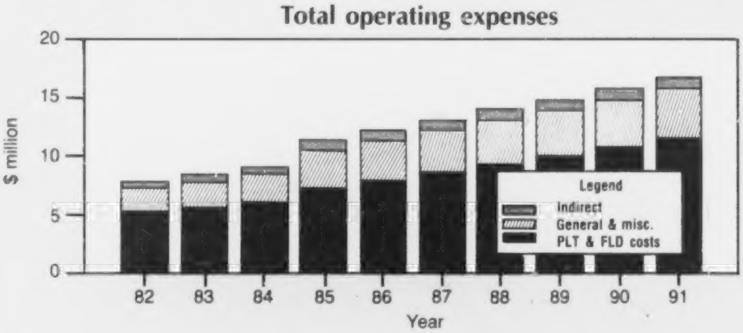
Raw gas volume, MMcfd

| | |
|---|---|
| 82 | 56.0 |
| 83 | 67.0 |
| 84 | 78.0 |
| 85 | 84.0 |
| 86 | 81.0 |
| 87 | 77.0 |
| 88 | 72.0 |
| 89 | 66.0 |
| 90 | 59.0 |
| 91 | 51.0 |



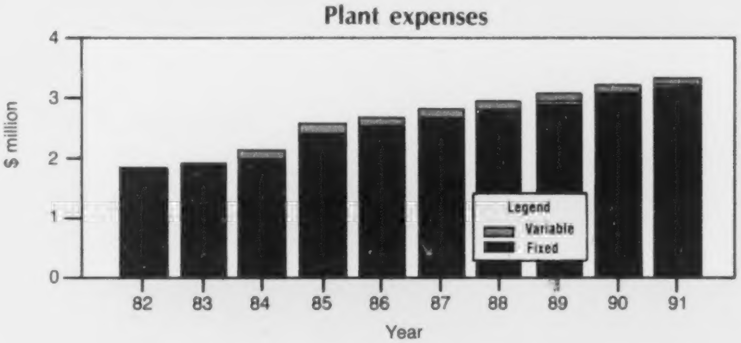
Operating expenses,
$ thousands

| | |
|---|---|
| 82 | 7945.0 |
| 83 | 8483.0 |
| 84 | 9126.0 |
| 85 | 11438.0 |
| 86 | 12260.0 |
| 87 | 13089.0 |
| 88 | 13961.0 |
| 89 | 14867.0 |
| 90 | 15784.0 |
| 91 | 16753.0 |



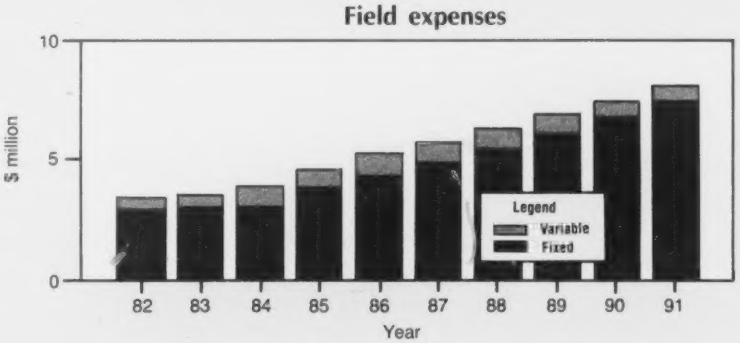
Total plant expenses,
$ thousands

| | |
|---|---|
| 82 | 1834.0 |
| 83 | 1933.0 |
| 84 | 2127.0 |
| 85 | 2561.0 |
| 86 | 2683.0 |
| 87 | 2810.0 |
| 88 | 2942.0 |
| 89 | 3076.0 |
| 90 | 3215.0 |
| 91 | 3357.0 |



Total field expenses,
$ thousands

| | |
|---|---|
| 82 | 3511.0 |
| 83 | 3751.0 |
| 84 | 3999.0 |
| 85 | 4792.0 |
| 86 | 5330.0 |
| 87 | 5866.0 |
| 88 | 6436.0 |
| 89 | 7028.0 |
| 90 | 7623.0 |
| 91 | 8259.0 |



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throughput volumes to arrive at the total cost.

The primary aim in preparing the financial analysis section is to calculate the actual cash flow of a facility. Therefore, ACRS-type depreciation and investment tax credits are used for the purpose of calculating taxes. No charges are made for deferred income taxes.

If desired, the format of the economic model also allows for financial calculations, such as financial net income, and return on assets. In this case, the last two sections, financial analysis and economics, are combined. The depreciation method is changed, if necessary, to reflect company policy.

Indirect charges, depreciation, and taxes are again subtracted from the Ibirt to arrive at net income. The average undepreciated investment in a facility, or average capital employed, is calculated for each year using historic investments plus incremental investments, working capital, less depreciation. Return on assets is calculated by dividing the financial net income by the average capital employed in the facility for the current year. Economic measures of merit, such as average annual rate of return (AARR), number of times expenditure returned (NTER), and payout, may be calculated on the incremental investments.

It should be noted that if a facility has matured completely and nonincremental growth is expected, the existing connected reserves section is equivalent to total reserves production, and no further work is required.

However, for plants with expected future growth, the future connected reserves model must be prepared. This provides the basis for comparing the inherent position in a facility to the growth potential. Assembling this section of the model requires much consideration since forecasts of future drilling and well connection activity in the gathering system, as well as future capital requirements in the plant and system, are included.

Finally, projections used in both the existing connected reserves and future connected reserves sections are based on existing operations and contractual agreements of a facility. Proposed changes in contracts or operations should not be included since the overriding premise is to predict future trends under existing conditions.

**Reporting results.** The economic models per se consist of four worksheets with identical formats. The first worksheet contains the historic production and existing connected reserves sections. The second is the future connected reserves model.

## The authors. . .

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Panatier received BS and MS degrees in mechanical engineering from Utah State University and will receive an MBA from Oklahoma State University in 1986. He is a member of ASME, NSPE, and The Society of Petroleum Engineers.

Dennis A. Stell has worked for Phillips Petroleum Co. since 1977 in a number of locations and capacities. He currently is the director of project evaluation for the gas and gas liquids group, Bartlesville. His responsibilities include the economic modeling program employed by Phillips plus economic evaluations of major gas gathering and processing projects. Stell graduated from New Mexico State University with a BS degree in chemical engineering.

The third worksheet combines the results of the first two, resulting in the facility's total reserves model on a cash flow basis. The fourth worksheet is also the total reserves model, but on a financial basis.

Graphics are particularly good for indicating trends and summarizing economic results. Many formats for these graphs are possible, depending on which information is selected for presentation.

One (Fig. 2) presents volume data and economic results on a cash flow basis. Financial results are shown in Fig. 3.

Fig. 4 is a detailed analysis of a facility's operating costs.

General information sheets are also prepared on each facility (Table 2). These have proven to be a valuable source of data including: operating statistics, disposition of residue gas and plant products, summaries of gas purchase contracts and residue sales contracts as well as financial data and a limited economic section. Also included are the major premises used in constructing the model, conclusions formed from the model's results, recommendations for improving profitability, and areas indicated for further work.

**Consolidation of results.** A major asset to economic modeling is that all plant and system models have the same format. This allows the data from individual plants to be combined into regions, divisions, or even company-wide totals.

This information is much more accurate than other projections that are essentially straight line extrapolations of past performance. It also provides calculated values for each data element of the individual plant model on a regional or company-wide basis, which is a feature that is not possible from macro-type modeling.

**Practical applications.** The first and most important use of the economic models is in trend analysis. This early warning system can result in timely contractual changes and modifications to operating conditions which provide improvements in profitability.

The models also make a good comparative tool to decide where best to use limited resources. By providing expected rates of return on incremental investments in each plant and system, decisions can be easily reached on where to invest in additional well connections and plant modifications and/or expansions.

The wide range of information contained in the economic models is often not available elsewhere in a single source. Essentially all operations from the wellhead to the tailgate of the plant are included. They can be used to solve a wide variety of problems and to answer a host of questions.

Proposed changes in plant and field operations and contracts can be evaluated using the appropriate section of the model. Since they are based on the actual historic performance of the facility, sensitivity to prices and modes of operation can be quickly and accurately analyzed.

Budget forecasting for operations and capital investment is improved. The projections are prepared on individual systems and plants and then combined to arrive at the total figures for the company.

Valuation analysis is greatly simplified. Both the existing facilities and future growth potential are combined into the same model. This is important in arranging credit for ongoing concerns or in preparing to sell assets.

Finally, the models are an excellent educational tool for both the engineers who prepare the models and management personnel who review the results.

• Since they encompass all areas of operations, accounting, and economics of individual facilities, as well as comparisons between plants and systems, the models provide insights not otherwise available. •

# Pinch technology guides retrofit

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**P**inch technology has been employed for the retrofit to a modern ethylene process. As a result, approximately 25% of the overall utility operating cost can be saved.

Pinch technology concepts for energy recovery have been used extensively within Union Carbide for several years, with outstanding results.[1] The technology has evolved from a novel energy conservation tool into a powerful methodology for realizing the full practical potential of a process with correct placement of unit operations and utilities.

When considering new designs, the technology is particularly useful in reducing both capital and operating costs. For retrofit designs, recent research[2] has evolved improved techniques for considering capital cost trade-offs vs. operating costs.

A detailed example relating to part of an ethylene process should help to demonstrate how the technology works. In the original blueprint for the plant (Fig. 1), feed to Column 1 comes from other separations in the process. The primary product is recovered in the overhead of Column 1 and heated before being used downstream.

Column 2 is used to recover any losses of the primary product from the tails of Column 1. The overhead of Column 2 is recycled to Column 1. A secondary product is recovered in the overhead of Column 3. The tails from Column 3 are recycled to both other columns.

Apart from conventional reboilers and condensers, the original design required additional heating and cooling loads:

- Heating of primary products prior to downstream consumers (Q = 13.3 units of heat).
- Cooling of recycle from Column 3 tails (Q = 7.1 units of refrigeration).
- Cooling of Column 1 tails before feeding to Column 2 (Q = 3.0 units of refrigeration).
- Heating of recycle from overhead of Column 2 (Q = 2.6 units of heat).

All these duties were to be achieved with separate heat exchangers.

Table 1

## Economics—original improvement

| | |
|---|---|
| Installed cost, $ | 150,000 |
| Estimated savings, $/year | 200,000 |
| Payback, months | 9 |

Before the plant was built, a proposal was developed to change the design. In this modification, the feed to Column 2 would be cooled with the overhead recycle from Column 2 (Fig. 2). The economics of this project were attractive, with a simple project payback of 9 months (Table 1). One additional heat exchanger was required. The original refrigeration heat exchanger was maintained for start-up and upsets. The proposal was accepted.

Recently, a pinch technology study was completed on the total process. Hot and cold streams can be combined on a temperature-enthalpy chart (Fig. 3). The hot composite is always hotter than the cold composite by at least a minimum permissible temperature difference ($\Delta T_{min}$).

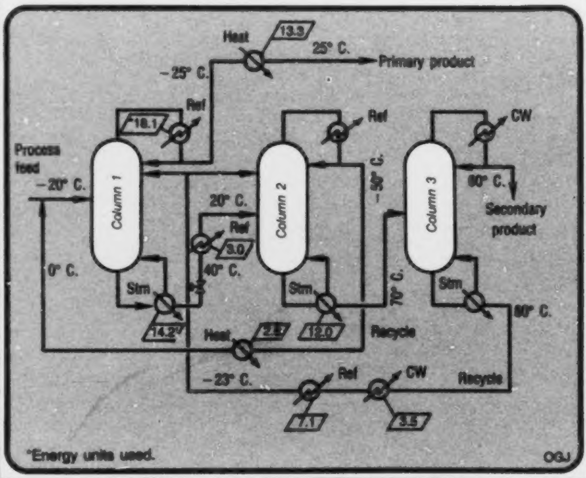
The horizontal overlap between the curves represents the maximum potential for process-to-process heat transfer. The remaining heat required by the cold composite represents the minimum, or target, hot utility. Similarly, the cold utility required to absorb the excess heat from the hot composite represents the minimum, or target, cold utility. The point where the curves come closest together is known as the process "pinch."

The key concept of pinch technology is that heat transfer across the pinch must be avoided. A design with no heat transfer across the pinch is guaranteed to achieve the hot and cold energy targets.[3]

On the actual composite curves for the process segment (Fig. 4), several pinches or near pinches were identified. Once all the process pinches and utility pinches have been identified,

Fig. 1

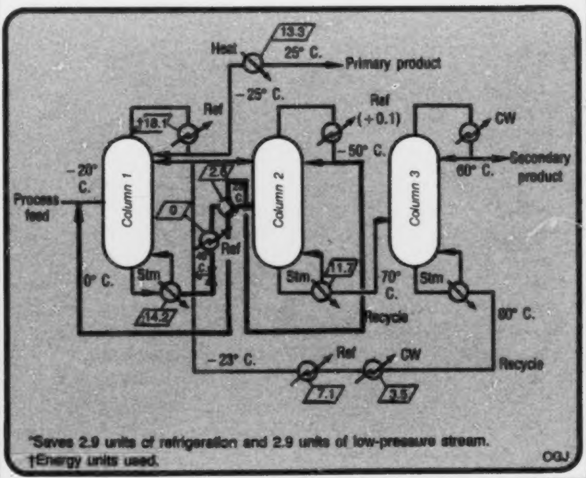
## Original design



*Energy units used.

Fig. 2

## As installed



*Saves 2.9 units of refrigeration and 2.9 units of low-pressure stream.
†Energy units used.

Fig. 3

Generalized composite curves

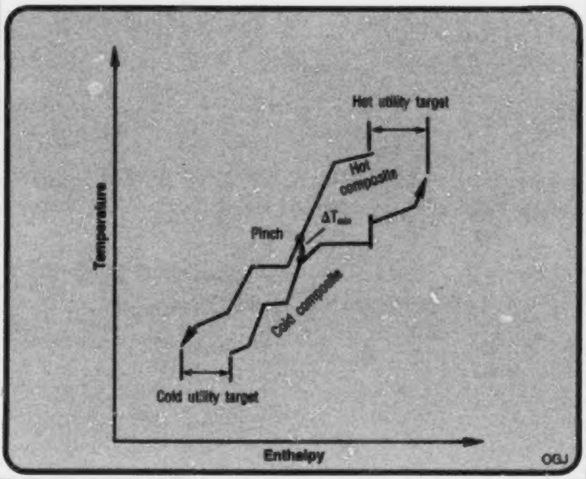
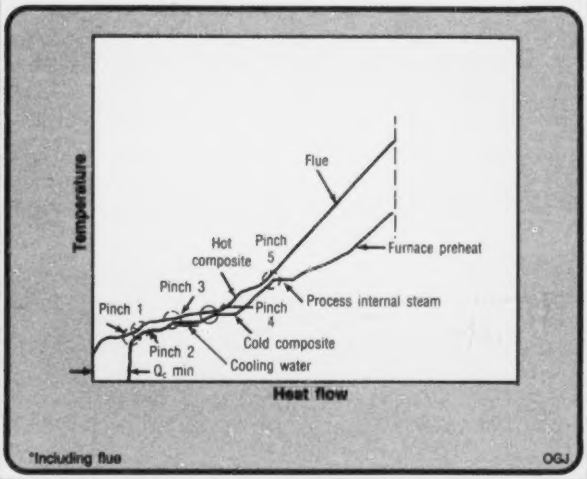


Fig. 4

Plant composite curves*



*Including flue

the streams can be represented on a grid diagram (Fig. 5).

On the grid diagram, process or utility pinches are shown as vertical lines with the pinch temperatures located at the top. Hot streams are represented as horizontal lines, from left to right. Similarly, cold streams are shown as horizontal lines, from right to left. Heat exchangers are shown as circles connected by vertical lines. Circles connected by a diagonal line indicate cross-pinch heat exchangers that cause excess utility consumption.

The grid diagram in Fig. 6 shows the effect of the added heat exchanger, as installed. From a pinch technology perspective, the effect of this improvement relative to the original design is that heat is transferred again across a pinch by the added heat exchanger.

This implies that there is still potential for improvement in overall utility consumption. What appeared to be an attractive project, when viewed locally, actually closed doors to further potential utility savings for the overall process.

By applying pinch technology concepts to a retrofit for the existing plant, a revised grid was developed (Fig. 7). Essentially, the cross pinch heat exchangers were replaced by correct heat exchangers, a straight forward action determined by pinch technology.

In detail, the retrofit proposal was to modify the process to accept a hotter feed to Column 2, resulting in steam savings on the reboiler for Column 2 with only a small increase in the refrigeration duty on the overhead condenser.

In the revised process flow diagram (Fig. 8), recyle from the overhead of Column 2 is heated by exchanging with the tails recycle from Column 3. Additional cooling of Column 3 tails recycle is accomplished by exchanging heat with the primary product from the overhead of Column 1.

The retrofit proposal was attractive (Table 2). It was one of 13 projects identified in an overall pinch technology study of the ethylene process. Had the pinch-based proposal been identified before the plant was built, even more money would have been saved (Table 3).

**Process description.** In the overall ethylene process, how the utilities interact with the process (Fig. 9) is important. Utilities are both generated and consumed within the process. External utilities are both imported and exported.

This particular study has significant

Fig. 5

Grid representation

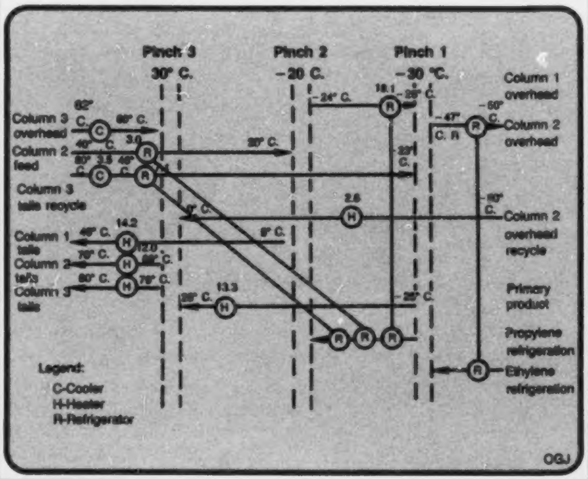

Pinch 3
30° C.
Pinch 2
−20 C.
Pinch 1
−30 °C.
Column 1 overhead
Column 3 overhead
Column 2 feed
Column 3 tails recycle
Column 2 overhead
Column 2 overhead recycle
Column 1 tails
Column 2 tails
Column 3 tails
Primary product
Propylene refrigeration
Ethylene refrigeration
Legend:
C-Cooler
H-Heater
R-Refrigerator
OGJ

Fig. 6

Grid representation as installed

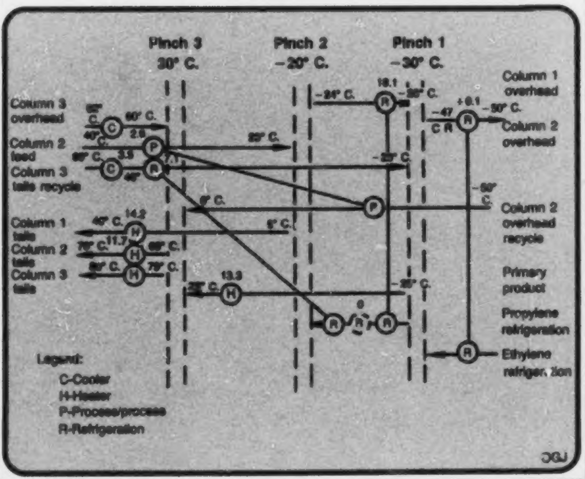

Pinch 3
30° C.
Pinch 2
−20° C.
Pinch 1
−30° C.
Column 1 overhead
Column 3 overhead
Column 2 feed
Column 3 tails recycle
Column 2 overhead
Column 2 overhead recycle
Column 1 tails
Column 2 tails
Column 3 tails
Primary product
Propylene refrigeration
Ethylene refrigeration
Legend:
C-Cooler
H-Heater
P-Process/process
R-Refrigeration
OGJ

Fig. 7

Pinch technology grid

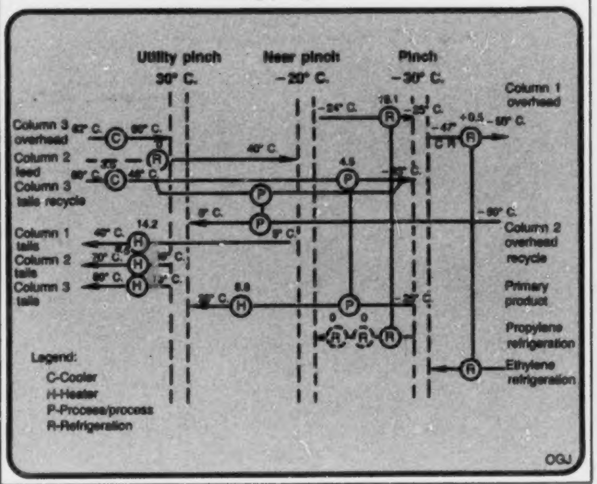
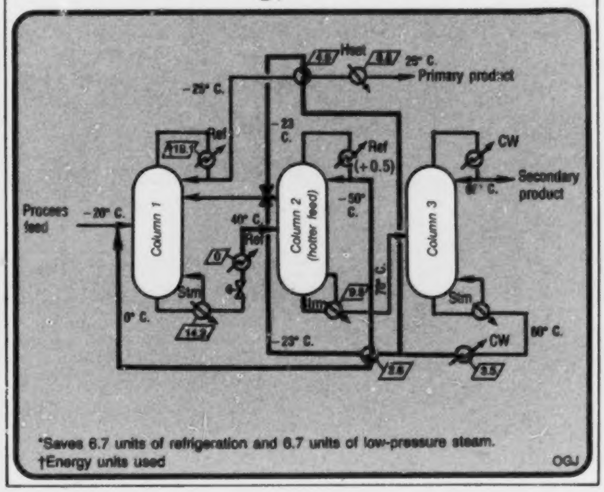

Utility pinch
30° C.
Near pinch
−20° C.
Pinch
−30° C.
Column 3 overhead
Column 2 feed
Column 3 tails recycle
Column 1 tails
Column 2 tails
Column 3 tails
Column 1 overhead
Column 2 overhead recycle
Primary product
Propylene refrigeration
Ethylene refrigeration
Legend:
C-Cooler
H-Heater
P-Process/process
R-Refrigeration
OGJ

Fig. 8

Pinch technology flow sheet*


Heat
25° C.
Primary product
−25° C.
−23 C.
Ref
(+0.5)
CW
Secondary product
Process feed
−20° C.
Column 1
Column 2 (hotter feed)
Column 3
40° C.
−50° C.
Stm
0° C.
−23° C.
60° C.
19.1
14.2
9.8
3.5
OGJ

*Saves 6.7 units of refrigeration and 6.7 units of low-pressure steam.
†Energy units used

benefit for two very important reasons:

- The process is heavily energy intensive, with broad process conditions from hot furnaces to refrigeration systems.
- The process is complex, involving multiple utilities, both generated and imported; heat and power integration within the process, furnaces, multilevel refrigeration systems, complex heat recovery in the overall process, a broad range of feed and cracking conditions, and a broad range of separation operating conditions.

The process cracks a varying range of feedstocks. The cracked furnace gas is primarily quenched by generating high-pressure steam.

Subsequent quench occurs via direct contact with oil in a gasoline fractionator. Water is removed in a quench tower. Furnace gas is compressed for acid gas removal and subsequent low temperature separation.

Several utility levels are included (Fig. 9). Steam for the furnace gas compressor is raised by quenching the cracked furnace gas. The steam is superheated in an auxiliary fired furnace before driving the first turbine on the furnace gas compressor.

High-pressure steam is extracted from the first turbine, superheated in the auxiliary furnace, mixed with imported, superheated high-pressure steam, and used to drive the second turbine on the furnace gas compressor. Intermediate pressure steam is extracted from the second turbine with a portion being used in the process and the remainder being exported to other plant consumers.

Additionally, a small quantity of high-pressure steam is used to drive a helper turbine on one refrigeration compressor. The extracted low-pressure steam from these sources is also used in the process. Within the process, two levels of steam are generated, and one hot water cycle is utilized. Two refrigeration compressors are driven by electric drives. One compressor operates a propylene refrigeration cycle. The other operates an ethylene cycle.

**Setting targets.** Prior to targeting, correct data extraction must be established. For the ethylene process, some utilities must be included as part of the process in the composite curves due to their complex interaction with the process. For instance, low-pressure steam used as feedstock-dilution steam must be considered as part of the process data since it is consumed within the process (Fig. 10).

Conversely, very-high-pressure steam generated as part of the furnace

Fig. 9

Process utility flowsheet

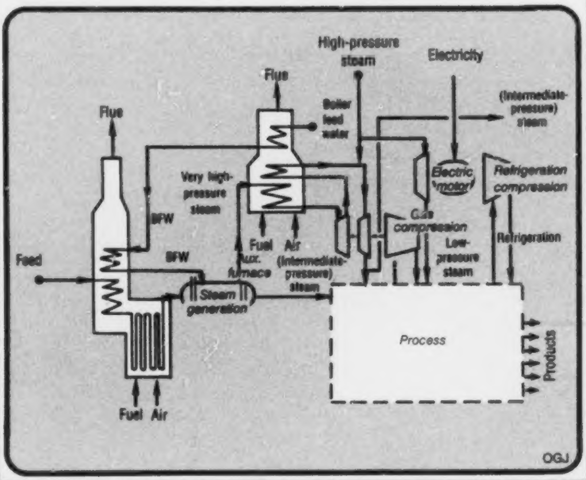

High-pressure steam
Electricity
Flue
Flue
Boiler feed water
(Intermediate-pressure) steam
Very high-pressure steam
Electric motor
Refrigeration compression
BFW
BFW
Gas compression
Refrigeration
Feed
Fuel
Air
Aux. furnace
(Intermediate-pressure) steam
Low-pressure steam
Steam generation
Process
Products
Fuel
Air
OGJ

Fig. 10

Composite curves with LP steam

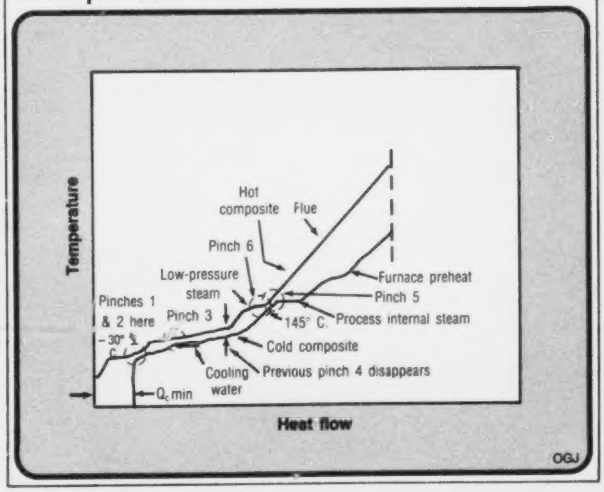


Table 2

## Pinch technology retrofit

| | |
|---|---|
| Installed cost, $ | 300,000 |
| Estimated savings, $/year | 450,000 |
| Payback, months | 8 |

Table 4

## Utility targets

| | Actual heat* | Predicted cost savings |
|---|---|---|
| | % | |
| Hot utility | 107 | 30 |
| Cooling water | 107 | nil |
| Refrigeration | 139 | 26 |
| **Total** | **111** | **29** |

*As % of target.

Table 3

## Cost comparison

| | Capital, $ thousand | Energy, $thousand/year | Payback, months | Comments |
|---|---|---|---|---|
| Blueprint design | 2,100 | 1,100 | — | Fig. 1 |
| Plant as installed | +150 | −200 | 9 | Compare Table 1 |
| Pinch retrofit proposed (relative to plant as installed) | +300 | −450 | 8 | Compare Table 2 |
| "What if" (relative to blueprint design) | −700 | −650 | — | Missed opportunity |

Table 5

## Retrofit projects*

| | Reduction | | Scope remaining |
|---|---|---|---|
| | Heat | Cost | Heat |
| | % | | |
| Hot utility | 6 | 26 | 1 |
| Cooling water | 4 | nil | 3 |
| Refrigeration | 38 | 22 | 1 |
| **Total** | **10** | **25** | **1** |

*Achieving target payback

quench was not included in the steam data and neither was the relevant section of the cracked furnace gases which are used to raise the quench steam because the assumption was made that this steam will continue to be raised and to drive the gas compression train. The effect of relaxing this assumption will be shown later.

Cooling water is much cheaper than refrigeration and should be used as much as possible. But, can too much be used? When cooling water is included in the process stream data, the target for refrigeration decreases, and a double pinch occurs below cooling water temperature, i.e., approximately −20° C. and −30° C. This means that additional cooling water will not further reduce refrigeration duties. Instead, additional cooling water will result in increased hot utility requirements.

Low-pressure steam is available to the process from the helper turbine on the refrigeration compressor. When incorporated into the process data, the low-pressure steam forces a utility pinch at approximately 145° C. The previous process pinch at 70° C. is now subject to different economic trade offs. This portion of the process can now be opened up for more relaxed process/process heat exchange with greater driving forces, i.e., less area required.

Finally, the furnace must be considered as part of the integration of utilities into the total process. When properly integrated, the minimum furnace requirements can be targeted from the slope of the flue gas line, along with all other required hot utilities.[4] At this point, additional hot utility does not appear to be required. Once targets have been truly established, a comparison of actual consumption vs. target consumption reveals where excess heat is being supplied to the process. When a process is in complete enthalpy balance, resulting from target quantities of both hot and cold utilities and maximum process/process heat exchange, excess energy simply upsets this balance.

Excess heat must cascade down across multiple pinches and ultimately be offset by reduced input at lower temperatures or excess cold utilities. In essence, hot and cold utilities must balance out across all pinches.

Excess heat flows for this process are shown in simplified fashion in Fig. 11. All hot and cold streams are symbolized by only one stream each. Vertical dashed lines represent multiple pinches caused by utilities or from the process itself. Notice that part of

Fig. 11

Heat flows before retrofit

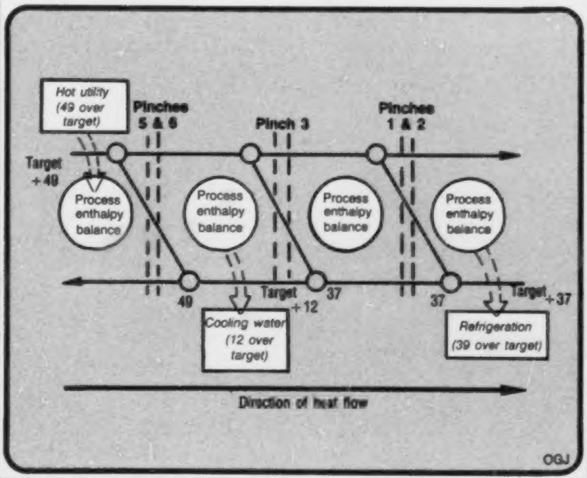


Fig. 12

Retrofit targets

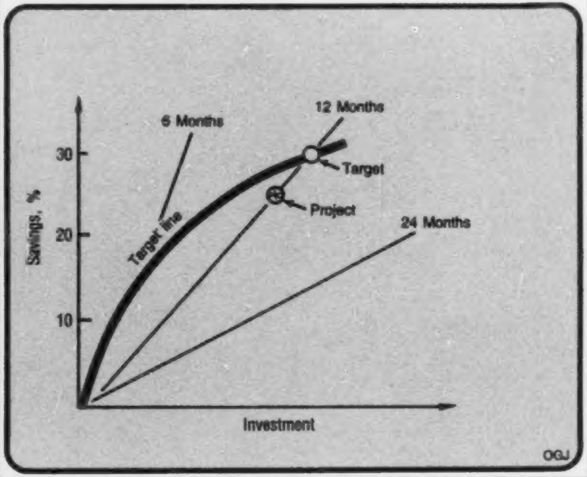


Fig. 13

Heat flows after retrofit

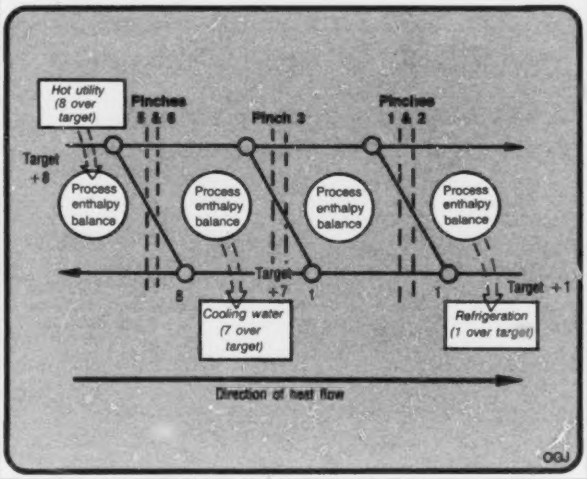
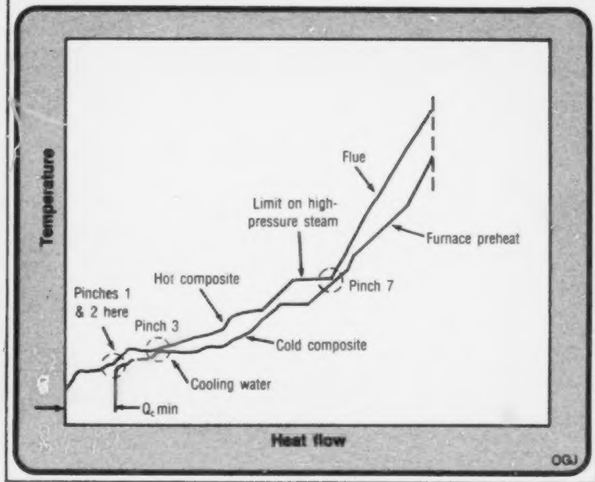


Fig. 14

Curves with HP steam available



the hot utility cascades to cooling water. The remainder ends up in excess refrigeration.

**Retrofit proposals.** In new design situations, pinch technology frequently identifies optimized minimum energy designs with reduced capital spending (Table 3). A retrofit design, by contrast, requires capital to correct existing problems.

The equivalent new design minimum can be achieved, but the project incremental economics tend to diminish the closer one approachs this minimum. In other words, some retrofit projects have extremely good project economics, with paybacks on the order of a few months or less. Other retrofit projects, especially those near the minimum target, will have less favorable economics, with paybacks on the order of several years or more.

This relationship between investment, savings, and payback can be explored for retrofit projects at the targeting stage.[2] For this plant, an economic targeting relationship emerges (Fig. 12). The project criterion was a marginal payback of 24 months. This determines the slope of the target line at the target point. The corresponding target savings are approximately 29% of current utility operating costs (Table 4). One of the important aspects of pinch technology is its ability to set cost trade offs for different scenarios working from the targets. This point is evident in Table 4 where a less expensive utility has been substituted for a more expensive utility. The result is large cost savings vs. the smaller percent reduction in actual heating values.

Fig. 13 shows the results after retrofit of the 13 proposals identified to correct cross-pinch heat flows. Table 5 lists the results on each utility.

Once again, cost savings are larger than the percentage reduction in heat flows due to the effect of costs on different utilities. All projects had very attractive payback economics. They have been incorporated into a plant cost reduction program already underway. The economic performance of the projects finally proposed is contrasted in Fig. 12 with the targets. Current utility operating costs will be reduced by 25%, rather than 29%, at a slightly lower investment than targeted. This accuracy is typical for targets set in the retrofit context.[2]

**Utility scenarios.** Every study has different specific requirements, relevant only to that particular location. For instance, different utilities, different pressure levels, and different operability requirements may totally change a situation, making two stud-

Fig. 15

HP steam generated

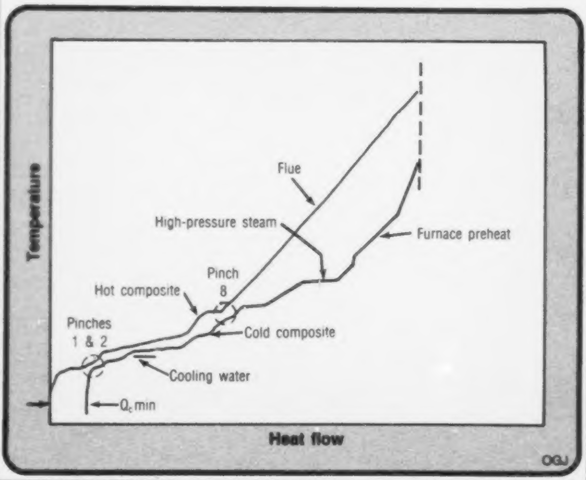


Fig. 16

LP steam not available

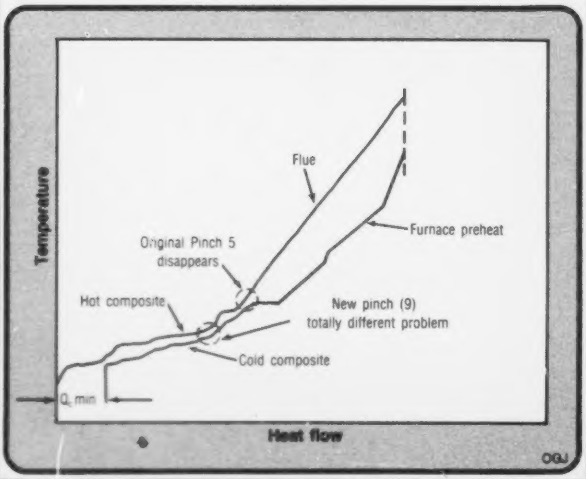


Fig. 17

Higher LP steam generated

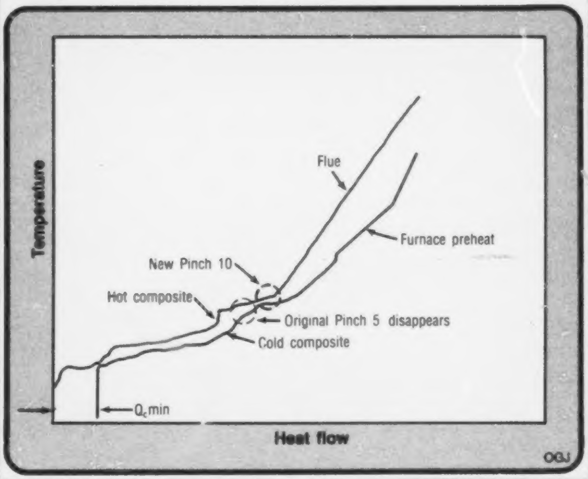
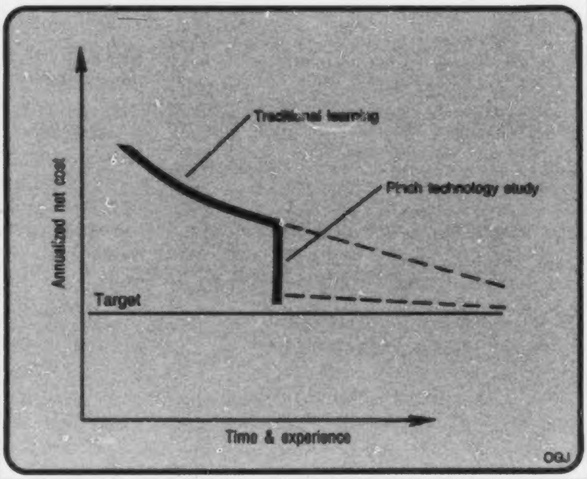


Fig. 18

Learning curve



## The authors. . .

**Linnhoff**

**Witherell**

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Linnhoff has 10 years of experience in the research and application of process design methods. He holds an MSc degree in mechanical engineering from the ETH Zurich and a PhD degree in chemical engineering from Leeds University, U.K.

W.D. Witherell is a staff engineer with Union Carbide Corp. He has over 16 years of industrial experience including extensive plant engineering activities and involvement in two major capital projects. For the last 3 years, Witherell has been a charter member of the Advent technology function at Carbide. He holds a BSChE degree from Virginia Polytechnic Institute and State University and an MBA degree from West Virginia University.

ies very dissimilar. Several process scenarios have to be studied and "what-if" questions addressed. The following section stresses by way of some simple examples what effect different assumptions regarding utilities would have had on the study results.

Fig. 14 illustrates what happens when the assumption that the available high-pressure steam is used to drive the furnace gas compressor is relaxed. Some of the high-pressure steam can be used, but only up to the point where a new pinch against the cold composite curve is created. Different economic trade-offs and different proposed network configurations would result. When additional high-pressure steam is generated from the process instead of being imported, the result is that the target hot utility must increase to accomplish the increased steam generation (Fig. 15). Also, perhaps less obvious, process integration at temperatures below steam raising becomes tighter.

Fig. 16 shows the effect of exporting the low-pressure steam which is available from the helper turbine. As discussed previously, the result is that the process pinch at around 70° C. returns, causing additional constraints in a now much tighter process.

Finally, if the LP steam from the helper turbine can be received at a higher pressure, a different utility pinch results (Fig. 17). The new pinch location in this example is as expected. However, this is not always the case. Ethylene processes have been in existence for a long time. Improvements have been significant. So, it may come as a surprise that the scope for improvement is still significant.

For this process, the minimum energy cost target has been clearly determined and projects identified to approach that target closely. Several of the 13 projects identified would not have been found otherwise.

Many ideas for energy conservation may appear to offer favorable project economics. The question is whether or not an idea is compatible with the concept of overall optimization. Pinch technology answers this question.

Every study is different. Individual results should not be directly applied to other, similar processes. Different utilities alone could lead to a totally different approach.

Studies involving multiple utilities, both imported and exported, are difficult. Incorrect data extraction, e.g., leaving out a utility, may seem minor. But results could be important.

A small error in data extraction may result in a significant difference in targeted utility levels and in perceived design complexity, either overstating the case or eroding incentives. This small error may make the difference between undertaking a project or not.

Above all, such an error may create a false sense of security by assuming the process is optimal when in fact it is not. In-depth experience is required to prevent costly mistakes.

Once a study is implemented there will be no surprises. Pinch targets are thermodynamically rigorous for process integration. Typically, pinch technology studies result in step changes on established learning curves (Fig. 18). This holds true even for mature technologies such as ethylene. Further improvements are probably not possible without new reactor or separator technology, new materials of construction, or some other major technological advance.

**References**

1. Linnhoff, B., and Vredeveld, D.R., "Pinch Technology has Come of Age," Chemical Engineering Progress, July 1984, pp. 33-40.
2. Tjoe, T.N., and Linnhoff, B., "Pinch Technology Retrofit: Setting Targets for an Existing Plant," Chemical Engineering, April 28, 1986.
3. Linnhoff, B., et. al., "A User Guide on Process Integration for the Efficient Use of Energy," The Institution of Chemical Engineers, George E. Davis Building, 165-171 Railway Terrace, Rugby CV21 3HG, U.K. (1982).
4. Linnhoff, B., "The Process/Utility Interface," Second International Meeting, Rational Use of Energy in Industry, Liege Belgium, Mar. 10-12, 1986.

# Packed tower program eases calculations for

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A packed tower program will calculate the diameter and hydraulics of a packed tower, or check the hydraulics of an existing tower for other process conditions. It is written in simple BASIC for an IBM PC and could easily be converted to other PC's.

There are approximately 100 statement lines, with memory requirement of approximately 4,100 bytes.

The program is presented as an aid, or tool, to reduce tedious calculations in design or revision work.

Much has already been written on the specifics of design methods and calculation procedures for packed towers. So this article will cover only the program's procedure and calculation method, input requirements, output data, and features.

The program first transforms the raw data into consistent units. Gas flowrate in pounds per hour is calculated from the input of standard cubic feet per minute and specific gravity, or moles per hour and molecular weight. Liquid flowrate in pounds per hour is calculated from the gallons per minute and specific gravity input.

Using the temperature, pressure, compressibility, and molecular weight inputs, the gas density in pounds per cubic foot is calculated from the ideal gas law equation. Liquid density is calculated directly from the specific gravity. With this data, the program then calculates the "x" ordinate of the generalized flooding correlation for packed towers. Using regressed design curves of X vs. Y, which somewhat parallel the flooding curve, the program calculates the Y abscissa function which relates liquid and gas densities, gas mass velocity, packing factor, gravitational constant, and liquid viscosity.

For each packing factor entry, the program proceeds to calculate tower diameter, gas and liquid mass velocities, percent flooding, and pressure drop.

The diameter is first calculated based on gas flowrate and gas mass velocity obtained from the Y function. The diameter is then adjusted to the nearest 0.25 ft. Gas and liquid mass velocities are then calculated using the respective flowrates and the adjusted diameter. Percent flooding is based on the ratio of adjusted gas mass velocity and the mass velocity at flooding conditions.

Pressure drop is calculated in several steps. A drop of 0.3 in. $H_2O$/ft is first assumed. From regressed formulas, constants for the generalized pressure drop correlation are calculated, and then used in the generalized correlation to calculate the pressure drop.

The calculated drop is compared to the assumed drop.

If it is not within 5%, the program prorates to a new assumed pressure drop and repeats the operation until the calculated drop is within 5% of the (new) assumed. If the pressure drop calculates to be below 0.05 in. or above 1.5 in., the printout will show only "less than 0.05 in." or "greater than 1.5 in."

In addition to diameter and the other data for each packing factor, the

Table 1

## Input data

Description of tower: Example C-102 gas scrubber
? C-101 MEA absorber
Tower dia., ft (enter 0 for diameter calc) ? 0
Enter gas flow either in scfm or mol/hr
Gas flow, scfm. If flow is in mol/hr, Enter 0? 11,200
Enter gas sp gr (air = 1.0)?0.58
Gas compressibility factor. Use 1 if unknown?0.98
Liquid flow, gpm? 310
Liquid sp gr? 1
Liquid viscosity, cps? 0.9
Temperature, °F.? 105
Pressure, psia? 445
Packing factors (PF) to be used. Enter 0 after last one
First PF? 85
Next PF? 52
Next PF? 28
Next PF? 0
Do you have another case, Y or N??

## Packed tower program

```
1  REM PROGRAM TO CALCULATE/RATE PACKED TOWERS (TOWER)
5  CLS:LOCATE 4,10:PRINT"This program will calculate diameter and hydraulics of
a";
10 PRINT"packed tower or check hydraulics of an existing tower":PRINT
15 F1=.5:Y1=62.4:Y2=.7854:Y3=4:F2=100:F3=1000:F4=10000:F5=17500:F6=30000
16 F7=.011:F8=.061
20 DEF FNF(A)=EXP(-3.8416-1.064*A-.1218*A^2)
25 DEF FNL(A)=EXP(-4.4527-.9875*A-.1379*A^2-.0079*A^3)
30 DEF FNO(A)=EXP(-4.9998-1.1027*A-.1825*A^2-.014*A^3)
40 PRINT"Description of Tower: Example  C-102 Gas Scrubber":INPUT A1$
45 INPUT"Tower Dia, Ft (enter 0 for Diameter calc)";DI
50 PRINT"Enter gas flow either in SCFM or Mol/Hr."
55 INPUT"Gas Flow, SCFM.  If  flow is in Mol/Hr., Enter 0";CFM
60 MH=0:MW=0:IF CFM=0 THEN 70
65 INPUT"Enter gas Sp.G (air=1.0)";SG:GOTO 75
70 INPUT"Gas Flow, Mol/Hr";MH:INPUT"Gas Mol Wt";MW:SG=0
75 INPUT"Gas Compressibility Factor. Use 1 if unknown";Z
80 INPUT"Liquid Flow, GPM";GM:INPUT "Liq Sp G";SL
85 INPUT"Liquid Viscosity,CPS";V
90 INPUT"Temperature, deg F";T:INPUT"Pressure, PSIA";P
100 PRINT"Packing factors to be used. Enter 0 after last one"
105 I=1:PRINT"First";
110 INPUT " PF";P(I):IF P(I)=0 THEN I=I-1:GOTO 120
111 IF I=5 THEN PRINT"Ok, that's enough":GOTO 120
115 I=I+1:PRINT"Next";:GOTO 110
120 LPRINT CHR$(14);CHR$(27)"-1";A1$:LPRINT CHR$(27)"-0"
125 LPRINT"Following is the data you gave me:":LPRINT
130 LPRINT"Specified Diameter,Ft:";DI
135 LPRINT"Gas Flow, SCFM:";CFM;"        Mol/Hr:";MH
140 LPRINT"Gas Sp G (Air=1.0):";SG;"    Mol Wt:";MW;"       Comp Factor:";Z
145 LPRINT"Liquid Flow,GPM:";GM"    Sp G:";SL;"    Viscosity,CPS:";V
150 LPRINT"Tower Temperature,deg F:";T;"      Pressure,PSIA:";P
155 LPRINT"Packing Factors:";
160 FOR K=1 TO I:LPRINT P(K);:NEXT K:LPRINT:LPRINT
180 MPH=MH:IF CFM>.1 THEN MPH=CFM/6.32
185 IF SG>.1 THEN MW=SG*29
190 PG=INT(MW*MPH+F1):RG=INT(MW*P*93.36/((460+T)*Z)+F1)/1000!
200 PL=INT(GM*SL*500+F1):X=INT(F3*PL*SQR(RG/(SL*Y1))/PG+F1)/F3
210 IF X<F7 THEN GOSUB 465:LPRINT:GOTO 235
215 IF X<F8 THEN GOSUB 470:LPRINT:GOTO 235
220 IF X>Y3 THEN GOSUB 475:LPRINT
235 Y=LOG(X):IF DI>.1 THEN 355
245 LPRINT "Tower loadings given.  Diameter & hydraulics to be calculated....."
250 LPRINT:GOSUB 410
255 FOR K=1 TO I:PF=P(K)
260 Y5=FNL(Y):GOSUB 500:IF XL<F5 THEN 275
265 Y5=FNO(Y):GOSUB 500:IF XL<F6 THEN 275
270 Y5=.9*FNO(Y):GOSUB 500
275 AO=INT(F4*Y5+F1)/F4:N=AO:GOSUB 450:AO$(K)=N$:GOSUB 510:NEXT K
280 AA=INT(F4*FNF(Y)+F1)/F4:LPRINT:LPRINT
300 LPRINT"   Liquid     Gas      Gas    Density          Curve Values"
```

# diameter, hydraulics of tower

Table 2

## Computer printout

```
C-101 MEA absorber
Following is the data you gave me:
Specified diameter, ft: 0
Gas flow, scfm: 11,200      mol/hr: 0
Gas sp gr (Air = 1.0): 0.58      Mol wt: 0      Comp factor: 1
Liquid flow, gpm: 310      sp gr: 1      Viscosity, cps: 0.9
Tower temperature, °F.: 105      Pressure, psia: 445
Packing factors: 85      52      28

Tower loadings given. Diameter & hydraulics to be calculated. . . .

 Diameter        (G)          (L)          % of                 Press drop,
    Ft         Lb/r/ft²     Lb/hr/ft²      flood        PF      in. H2O/ft
     4          2,372        12,334         70.1        85         0.56
     3.5        3,098        16,110         71.6        52         0.56
     3.5        3,098        16,110         52.5        28         0.27

 Liquid,      Gas,       Gas,      Density,   ---------Curve values---------
  lb/hr       lb/hr     mol wt     lb/cu ft    X, Ord    Y, flood   Y, design    PF
 155,000     29,808     16.82       1.237      0.732     0.0296     0.0156       85
 155,000     29,808     16.82       1.237      0.732     0.0296     0.0156       52
 155,000     29,808     16.82       1.237      0.732     0.0296     0.0093       28
End of calculations for this case.
```

```
305 LPRINT"    Lb/Hr     Lb/Hr    Mol Wt     Lb/Cf     X,Ord  Y,Flood  Y,Design
 PF"
310 N=PL:GOSUB 450:PL$=N$:N=MW:GOSUB 450:MW$=N$:N=RG:GOSUB 450:RG$=N$
315 N=X:GOSUB 450:X$=N$:N=AA:GOSUB 450:AA$=N$:N=PG:GOSUB 450:PG$=N$
325 FOR K=1 TO I:LPRINT PL$;PG$;MW$;RG$;X$;AA$;AO$(K):PF$(K):NEXT K
330 LPRINT:LPRINT "End of calculations for this case."
335 PRINT:PRINT:PRINT"Do you have another case, Y or N??"
340 D$=INKEY$:IF D$="y" OR D$="Y" THEN LPRINT:LPRINT:CLS:GOTO 40
345 IF D$="n" OR D$="N" THEN END
350 GOTO 340
355 LPRINT:LPRINT"Tower diameter given, hydraulics to be checked.....":LPRINT
360 GOSUB 410:D=DI:XL=INT(PL/(D^2*Y2)+F1)
365 G=INT(PG/(D^2*Y2)+F1)
370 FOR K=1 TO I:PF=P(K):Y5=PF*G^2/(4.17E+08*Y1*RG*SL):GOSUB 510:NEXT K
375 LPRINT:LPRINT "The above tabulation based on the given diameter."
380 LPRINT "My calculated diameter and hydraulics are as follows:"
385 LPRINT:GOTO 250
410 LPRINT"Diameter       (G)          (L)          % of                 Press Drop"
415 LPRINT"   Ft      Lb/Hr/Ft2  Lb/Hr/Ft2     Flood         PF     In.H2O/Ft"
420 RETURN
430 N$=STR$(N)
435 IF LEN(N$)<11 THEN N$=" "+N$:GOTO 435
440 RETURN
450 N$=STR$(N)
455 IF LEN(N$)<9 THEN N$=" "+N$:GOTO 455
460 RETURN
465 LPRINT"Are you kidding me? The above conditions are not normal for packed"
466 LPRINT"tower service. However I will continue to calculate.":RETURN
470 LPRINT"You have a vapor loaded tower. Try also a trayed tower.":RETURN
475 LPRINT"! Caution! You have a highly liquid-loaded tower.  Check this"
476 LPRINT"out and be sure to allow sufficient free area at support plate."
477 RETURN
500 D=SQR(PG/(SQR(4.18E+08*RG*(SL*Y1)^2*Y5/(V^.2*PF*Y1))*Y2))
505 D=INT(Y3*D+F1)/Y3:G=INT(PG/(D^2*Y2)+F1):XL=INT(PL/(D^2*Y2)+F1):RETURN
510 FL=SQR(4.18E+08*RG*SL^2*Y1*FNF(Y)/(V^.2*PF))
515 PC=INT(F3*G/FL+F1)/10:DP=.5
520 Y6=-1*(4.1405*DP^-.1317)
521 Y7=-1*(.6666*DP^5-4.2646*DP^4+9.3938*DP^3-8.952501*DP^2+3.6361*DP+.438)
522 Y8=-1*(.01976*DP^5-.1676*DP^4+.5170001*DP^3-.6975*DP^2+.3799*DP+.0632)
525 Y9=EXP(Y6+Y7*LOG(X)+Y8*(LOG(X))^2)
526 YD=Y5-Y9:IF ABS(YD/Y5)<.05 THEN 535
530 DP=(1+.75*YD/Y9)*DP:GOTO 520
535 DP=INT(F2*DP+.5)/F2
540 D$=STR$(D)
545 IF LEN(D$)<6 THEN D$=" "+D$:GOTO 545
550 N=G:GOSUB 430:G$=N$:N=XL:GOSUB 430:XL$=N$:N=PF:GOSUB 450:PF$(K)=N$
555 N=PC:GOSUB 430:PC$=N$:N=DP:GOSUB 430:L$=N$:IF DP<.05 THEN L$="   Less than .
05"
560 IF DP>1.5 THEN L$="    Greater than 1.5"
565 LPRINT D$;G$;XL$;PC$;PF$(K);L$:RETURN
```

Table 3

## Existing tower input data

```
Description of tower: Example C-102 gas
  scrubber
? C-102 gas scrubber
Tower dia. ft (enter 0 for diameter calc)?
  11.5
Enter gas flow either in scfm or mol/hr
Gas flow, scfm. If flow is in mol/hr, enter 0?
  0
Gas flow, mol/hr? 27,685.9
Gas mol wt? 17.35
Gas compressibility factor. Use 1 if
  unknown? 0.9
Liquid flow, gpm? 2,700
Liq sp gr? 0.787
Liquid viscosity, cps? 1
Temperature, °F.? 502
Pressure, psia? 1,150
Packing factors (PF) to be used. Enter 0
  after last one
First PF? 27
Next PF? 20
Next PF? 0
Do you have another case, Y or N??
```

program will print out liquid and gas flowrates in pounds per hour, gas molecular weight, gas density in pounds per cubic foot, and the X and Y values of the generalized correlation.

When an existing tower is to be checked with a given diameter, the program uses this diameter for calculation of the gas mass velocity. It then proceeds from this point to calculate liquid mass velocity, percent flooding, and pressure drop as already described.

After completing the existing diameter calculation, the program goes through the complete calculation as if for a new tower.

**Input.** The program prompts the user for the normal input data required for calculations as follows:

- Description of the tower for identification purposes.
- Diameter of the existing tower to be checked. 0 is entered for calculation of a new tower.
- Gas flowrate in standard cubic feet per minute or moles per hour.
- Gas specific gravity (air = 1) or molecular weight dependent on the flow units previously entered.
- Gas compressibility factor. Default value is 1 if unknown.
- Temperature and pressure for gas density calculation.
- Liquid flowrate, specific gravity, and viscosity.
- Packing factors to be used, up to 5 entries.

**Output.** The program first prints out a format of the input data so that input and the basis of design can be checked.

When calculating the diameter for a new tower, the program calculates and prints out the diameter, liquid and

Table 4

## Existing tower printout

```
C-102 gas scrubber

Following is the data you gave me:
Specified diameter, ft: 11.5
Gas flow, scfm: 0    Mol/hr: 27,685.9
Gas sp gr (Air = 1.0): 0     Mol wt: 17.35     Comp factor: 0.9
Liquid flow, gpm: 2,700     Sp gr: .787     Viscosity, cps: 1
Tower temperature, °F.: 502     Pressure, psia: 1,150
Packing Factors: 27     20

Tower diameter given, hydraulics to be checked. . . .

 Diameter,      (G)          (L)          % of                 Press drop,
    ft       Lb/hr/ft2    Lb/hr/ft2       flood        PF      in. H2O/ft
   11.5        4,625       10,229         60.6         27         0.26
   11.5        4,625       10,229         52.1         20         0.18

The above tabulation based on the given diameter.

My calculated diameter and hydraulics are as follows:

 Diameter,      (G)          (L)          % of                 Press drop,
    ft       Lb/hr/ft2    Lb/hr/ft2       flood        PF      in. H2O/ft
   10.5        5,547       12,270         72.6         27         0.57
    9.75       6,434       14,230         72.5         20         0.57

 Liquid,     Gas,      Gas,     Demsity,  ----------Curve values----------
  lb/hr      lb/hr    mol wt   lb/cu ft    X, ord    Y, flood   Y, design    PF
1,062,450  480,350    17.35     2.151      0.463     0.0453      0.023       27
1,062,450  480,350    17.35     2.151      0.463     0.0453      0.023       20
End of calculations for this case.
```

gas hydraulics, percent flooding, packing factor, and pressure drop for each packing factor entered.

The program then prints out the liquid and gas flows in pounds per hour, gas molecular weight and density, and the design curve values of the X ordinate, and Y flooding and Y design abscissas.

When checking an existing tower, the program prints out the given diameter with liquid and gas hydraulics, percent flooding, packing factor, and pressure drop for each packing factor entered.

Then the program calculates its version of the required diameter plus all data mentioned above for a new tower calculation.

### Program features

1. All meaningful data relative to a packed tower system are printed out for review and for comparison with existing calculation procedure.

2. A new tower can be calculated or an existing tower checked.

3. Gas flowrate input can be in standard cubic feet per minute or moles per hour, depending on data readily available.

4. More than one packing factor can be entered to check the effect on the tower.

5. Input prompts are friendly and define the units used in order to minimize entry errors.

6. Input data are printed out. In case of an odd calculation, the design basis can be easily checked.

7. Calculated tower diameter is adjusted to the nearest 0.25 ft. For example, if the calculated diameter is 3.19 ft., the printed diameter is 3.25 ft (3 ft, 3 in.).

8. Triggers are built-in to warn of process conditions which are not normal for packed tower use. In these cases, another type of tower should be used, or the system calculations should be hand checked.

Two examples of input and output are given. Tables 2 and 3 present the data and calculation results for a new tower, using three packing factors. Table 1 shows the total input data as it appears on the monitor screen. Table 2 shows the printed output. Tables 3 and 4 cover the data for checking an existing tower. Table 3 shows the screen input data. Table 4 shows the corresponding calculated output. •

### The author. . .

Petrarca

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# Procedure

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A method has been developed to estimate the eight constants of the Benedict-Webb-Rubin equation of state. Constants can be obtained for hydrocarbon gases and vapors or other substances which are nonpolar and do not associate.

The Benedict-Webb-Rubin equation of state is one of the more prominent equations of state. It has proven to be useful for providing a variety of thermodynamic properties of fluids, particularly light hydrocarbons.

It has been used frequently in large software packages for process design. It is also readily programmable on a scientific calculator for desk calculations.

Obtaining these eight constants from experimental data is quite tedious using conventional numerical analysis techniques. Although values of these constants are tabulated in the open literature for a few substances, constants for the gas or vapor under consideration cannot readily be found, or the range of conditions of the tabulated constants may not match the range of the application of interest.

The method presented will determine the constants for conditions typical of most process engineering applications without any computer programming. For applications involving unusual conditions, it may be appropriate to do additional computer calculations. Information is included to show how this can be done with a minimal amount of programming effort and computer time.

**Method development.** The Benedict-Webb-Rubin equation of state is written in its usual form:

$$P = \frac{RT}{V} + \left(RTB_o - A_o - \frac{C_o}{T^2}\right)\frac{1}{V^2} + (RTb - a)\frac{1}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{T^2V^3}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right) \quad (1)$$

Refer to the nomenclature box for

# estimates Benedict-Webb-Rubin constants

Table 1

## Data for the determination of dimensionless constants

| Range | $T_r$ | $P_r$ | $Z^0$ | $Z'$ |
|---|---|---|---|---|
| 1 | 0.55 | 0.01 | 0.9804 | −0.0314 |
|  | 0.65 | 0.05 | 0.9377 | −0.0772 |
|  | 0.70 | 0.1 | 0.8958 | −0.1161 |
|  | 0.80 | 0.2 | 0.8539 | −0.1160 |
|  | 0.90 | 0.4 | 0.7800 | −0.1118 |
|  | 0.93 | 0.6 | 0.6635 | −0.1662 |
|  | 0.97 | 0.8 | 0.5580 | −0.1647 |
|  | 1.00 | 1.0 | 0.2901 | −0.0879 |
| 2 | 1.00 | 1.0 | 0.2901 | −0.0879 |
|  | 1.00 | 1.2 | 0.2237 | −0.0609 |
|  | 1.00 | 1.5 | 0.2583 | −0.0678 |
|  | 1.01 | 1.0 | 0.4648 | −0.0223 |
|  | 1.01 | 1.2 | 0.2370 | −0.0473 |
|  | 1.01 | 1.5 | 0.2640 | −0.0621 |
|  | 1.02 | 1.2 | 0.2629 | 0.0227 |
|  | 1.02 | 1.5 | 0.2715 | −0.0524 |
| 3 | 1.05 | 1.2 | 0.4437 | 0.1059 |
|  | 1.05 | 5.0 | 0.6956 | −0.137 |
|  | 1.2 | 2.0 | 0.5605 | 0.199 |
|  | 1.2 | 3.0 | 0.5425 | 0.1095 |
|  | 1.3 | 2.0 | 0.6908 | 0.1991 |
|  | 1.3 | 3.0 | 0.6344 | 0.2079 |
|  | 1.5 | 1.2 | 0.8933 | 0.1055 |
|  | 1.5 | 5.0 | 0.8200 | 0.2309 |

Table 2

## Dimensionless Benedict-Webb-Rubin constants

| Range | ω | $D_1$ | $D_2$ | $D_3$ | $D_4$ | $D_5$ | $D_6$ | $D_7$ | $D_8$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.00 | 0.9582 | 4.1466 | 1.0087 | 1.2287 | 1.1212 | 0.3379 | 1.7940 | 1.0234 |
|  | 0.05 | 1.1275 | 4.2509 | 1.2337 | 1.1953 | 1.1350 | 0.3583 | 1.9678 | 1.0130 |
|  | 0.10 | 1.3068 | 4.3527 | 1.4746 | 1.1703 | 1.1351 | 0.3752 | 2.1246 | 1.0099 |
|  | 0.15 | 1.5244 | 4.4902 | 1.7236 | 1.1356 | 1.1490 | 0.3948 | 2.3094 | 1.0030 |
|  | 0.20 | 1.7879 | 4.6540 | 1.9978 | 1.1030 | 1.1577 | 0.4164 | 2.5046 | 1.0110 |
|  | 0.25 | 2.0121 | 4.7830 | 2.2772 | 1.0835 | 1.1701 | 0.4398 | 2.6941 | 1.0171 |
|  | 0.30 | 2.2518 | 4.9117 | 2.5785 | 1.0580 | 1.1939 | 0.4681 | 2.9095 | 1.0245 |
|  | 0.35 | 2.5104 | 5.0453 | 2.8981 | 1.0143 | 1.1892 | 0.4967 | 3.1179 | 1.0340 |
|  | 0.40 | 2.8060 | 5.2055 | 3.2317 | 0.9763 | 1.1953 | 0.5342 | 3.3313 | 1.0469 |
| 2 | 0.00 | 1.6670 | 3.7714 | 2.2698 | 0.7344 | 1.0771 | 0.1909 | 2.4019 | 0.6258 |
|  | 0.05 | 1.6420 | 3.7714 | 2.2895 | 0.7428 | 1.0771 | 0.1921 | 2.3942 | 0.6258 |
|  | 0.10 | 1.6121 | 3.7739 | 2.3212 | 0.7553 | 1.0765 | 0.1914 | 2.3763 | 0.6150 |
|  | 0.15 | 1.5776 | 3.7878 | 2.3796 | 0.7973 | 1.0783 | 0.1883 | 2.3827 | 0.6070 |
|  | 0.20 | 1.5254 | 3.8055 | 2.4291 | 0.8593 | 1.0779 | 0.1834 | 2.3792 | 0.6000 |
|  | 0.25 | 1.4831 | 3.8790 | 2.4813 | 0.9420 | 1.0559 | 0.1728 | 2.3722 | 0.5869 |
|  | 0.30 | 1.4960 | 3.9138 | 2.5784 | 1.0051 | 1.0498 | 0.1682 | 2.3546 | 0.5815 |
|  | 0.35 | 1.5109 | 3.9399 | 2.6676 | 1.1011 | 1.0735 | 0.1641 | 2.3136 | 0.5778 |
|  | 0.40 | 1.4749 | 3.9662 | 2.7380 | 1.2187 | 1.0877 | 0.1630 | 2.2802 | 0.5890 |
| 3 | 0.00 | 1.6563 | 4.0162 | 1.9326 | 1.1832 | 1.5503 | 0.1617 | 2.3102 | 0.5343 |
|  | 0.05 | 1.6914 | 4.0365 | 2.0029 | 1.2294 | 1.5189 | 0.1584 | 2.2024 | 0.5284 |
|  | 0.10 | 1.7439 | 4.0749 | 2.0890 | 1.2739 | 1.4880 | 0.1551 | 2.1139 | 0.5206 |
|  | 0.15 | 1.7963 | 4.1012 | 2.1803 | 1.3173 | 1.4519 | 0.1522 | 2.0054 | 0.5140 |
|  | 0.20 | 1.8441 | 4.1294 | 2.2909 | 1.3675 | 1.4079 | 0.1503 | 1.9106 | 0.5150 |
|  | 0.25 | 1.8969 | 4.1504 | 2.4140 | 1.4207 | 1.3615 | 0.1500 | 1.7997 | 0.5222 |
|  | 0.30 | 1.9528 | 4.1621 | 2.5489 | 1.4731 | 1.3128 | 0.1510 | 1.6798 | 0.5352 |
|  | 0.35 | 2.0202 | 4.1805 | 2.6905 | 1.5345 | 1.2661 | 0.1511 | 1.5391 | 0.5443 |
|  | 0.40 | 2.0848 | 4.1751 | 2.8524 | 1.6018 | 1.2244 | 0.1511 | 1.3817 | 0.5504 |

Table 3

## Calculated values of the constants for ethane

|  | Range 1 | Range 2 | Range 3 |
|---|---|---|---|
| $A_0$ (l/g-mole)$^2$, atm | 4.4801 | 3.8879 | 4.1966 |
| $B_0$ (l/g-mole) | 0.05342 | 0.06632 | 0.07161 |
| $C_0$ (l/g-mole)$^2$, °K.$^2$, atm | 140800. | 222900. | 200396. |
| a (l/g-mole)$^3$, atm | 0.1709 | 0.1621 | 0.2244 |
| b (l/g-mole)$^2$ | 0.007040 | 0.004536 | 0.007646 |
| c (l/g-mole)$^3$, °K.$^2$, atm | 29760. | 33390. | 29750.0 |
| α (l/g-mole)$^3$ | 0.001031 | 0.0005556 | 0.0003256 |
| γ (l/g-mole)$^2$ | 0.02159 | 0.01315 | 0.01113 |

the definition of terms.

Next, both sides of the equation are divided by P, the absolute pressure. Put all terms on the left-hand side of the equation and introduce the reduced pressure ($P_r = P/P_c$), reduced temperature ($T_r = T/T_c$), and reduced volume ($V_r = V/V_c$). The result is:

$$1 - \frac{RT_cT_r}{P_cP_rV_cV_r} - \frac{RT_cT_rB_o}{P_cP_rV_c^2V_r^2}$$

$$+\frac{A_o}{P_cP_rV_c^2V_r^2} + \frac{C_o}{T_c^2T_r^2P_cP_rV_c^2V_r^2}$$

$$-\frac{RT_cT_rb}{P_cP_rV_c^3V_r^3} + \frac{a}{P_cP_rV_c^3V_r^3}$$

$$-\frac{a\alpha}{P_cP_rV_c^6V_r^6}$$

$$-\frac{c}{P_cP_rT_c^2T_r^2V_c^3V_r^3}$$

$$\left(1 + \frac{\gamma}{V_c^2V_r^2}\right) \exp\left(-\frac{\gamma}{V_c^2V_r^2}\right) = 0 \quad (2)$$

Next, combine the Benedict-Webb-Rubin constants with other constant quantities of critical temperature, pressure, volume, and the ideal gas constant by defining the following new constants:

$$D_1 = \frac{RT_cB_o}{P_cV_c^2} \quad (3)$$

$$D_2 = \frac{A_o}{V_c^2P_c} \quad (4)$$

$$D_3 = \frac{C_o}{V_c^2P_cT_c^2} \quad (5)$$

$$D_4 = \frac{RT_c{}^b}{P_cV_c^3} \quad (6)$$

$$D_5 = \frac{a}{P_cV_c^3} \quad (7)$$

$$D_6 = \frac{a\alpha}{P_cV_c^6} \quad (8)$$

$$D_7 = \frac{c}{P_cT_c^2V_c^3} \quad (9)$$

$$D_8 = \frac{\gamma}{V_c^2} \quad (10)$$

With the new constants, Equation 2 becomes

$$\left[1 - \frac{T_r}{P_rV_rZ_c} - \frac{T_rD_1}{V_r^2P_r} + \frac{D_2}{V_r^2P_r}\right.$$

$$+ \frac{D_3}{T_r^2V_r^2P_r} - \frac{T_rD_4}{V_r^3P_r} + \frac{D_5}{V_r^3P_r}$$

## Nomenclature

| | |
|---|---|
| $A_o$, $B_o$, $C_o$ | Constants in the Benedict-Webb-Rubin equation of state |
| D | Dimensionless constants in the Benedict-Webb-Rubin equation of state |
| P | Absolute pressure |
| R | Gas constant |
| T | Absolute Temperature |
| V | Molar volume |
| Z | Compressibility factor |
| a, b, c | Constants in the Benedict-Webb-Rubin equation of state |

**Greek letters**

| | |
|---|---|
| $\alpha$, $\gamma$ | Constants in the Benedict-Webb-Rubin equation of state |
| $\Delta$ | Value of the artificial objective function |
| $\omega$ | Pitzer accentric factor |

**Subscripts**

| | |
|---|---|
| b | Normal boiling point |
| c | Critical point |
| r | Reduced property |

$$- \frac{D_6}{V_r^6P_r} - \frac{D_7}{T_r^2V_r^3P_r}\left(1 + \frac{D_8}{V_r^2}\right)$$

$$\exp\left(- \frac{D_8}{V_r^2}\right)\Bigg] = 0 \qquad (11)$$

To solve for $D_1$ through $D_8$, eight sets of values of reduced temperature, pressure, and volume are needed to yield eight equations and eight unknowns. They are obtained in the following fashion.

Eight values of reduced pressure and temperature are specified. To obtain the corresponding values of reduced volume, the relationship between reduced volume and compressibility functions Z° and Z′ can be utilized.

$$V_r = (Z^\circ + \omega Z')\,T_r/(Z_cP_r) \qquad (12)$$

The critical compressibility is given by:

$$Z_c = 0.2901 - 0.0879\,\omega \qquad (13)$$

The compressibility functions Z° and Z′ are dependent upon reduced temperature and pressure, and tabulations for them have been prepared using experimental data.[1]

The Pitzer accentric factor, ω, is also a physical property, and for ordinary nonpolar materials it ranges from 0 to about 0.4. Extensive tabulations are available for it. It can be estimated several ways. One simple yet accurate expression is:[2]

$$\omega = \left(\frac{3}{7}\right)\frac{T_b/T_c}{1 - T_b/T_c}\log P_c - 1 \qquad (14)$$

**Solution.** The solution of the eight simultaneous nonlinear equations for $D_1$ through $D_8$ can be easily done using a method previously described by Kerr.[3] The left-hand sides of the eight equations (the bracketed term in Equation 11) are squared and summed to form an artificial objective function:

$$\Delta = \sum_{i=1}^{8} [\text{left-hand side of Eq. 11}]^2 \qquad (15)$$

### The author. . .

**Kerr**

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Kerr is a member of AIChE and the American Society for Engineering Education. He received a PhD in chemical engineering from Louisiana State University and he is a registered professional engineer in Tennessee and Louisiana.

The constants, $D_1$ through $D_8$, are manipulated by an optimum seeking method to drive Δ to zero or sufficiently close to zero. This exercise was performed for values of the accentric factors from 0 to 0.4 at intervals of 0.05, and for three ranges of values of reduced temperature, reduced pressure, Z°, and Z′.

The values of these variables that were selected or determined are shown in Table 1. Range 1 was chosen for use up to the critical point, Range 2 was chosen for use around the critical point, and Range 3 is for high temperatures and pressures.

These three ranges cover about two-thirds of the data in the compressibility tables for gases and vapors. The results of these calculations are shown in Table 2.

To use this table, the region of interest and the accentric factor are first determined. Values of $D_1$ through $D_8$ are obtained from the table and substituted into Equations 3 to 10 along with the critical properties to solve for the Benedict-Webb-Rubin constants in a sequential fashion.

Any consistent set of units can be used. The only exception is that critical pressure must be expressed in atmospheres when using Equation 14 to estimate the accentric factor.

It has been determined that by solving for the constants over these three ranges, the goodness of fit of the compressibility data has been improved.

**Application.** To illustrate the method, it is applied to ethane vapor. The critical temperature, pressure, and volume of ethane are respectively 305.4° K., 48.2 atm, and 148 cc/g-mole; the Pitzer accentric factor is 0.098.

Values of $D_1$ through $D_8$ of 1.2996, 4.3486, 1.4650, 1.1713, 1.1351, 0.3745, 2.1183, 1.0100 for Range 1 are obtained by interpolation of Table 2.

Next, using these values of the D's, values of $B_o$, $A_o$, $C_o$, b, a, α, c, and γ are solved sequentially from Equations 3 through 10.

The procedure is repeated for Ranges 2 and 3. The results are shown in Table 3.

Experimental PVT data for ethane vapor have been tabulated in the literature.[4] The average difference between these data and that predicted by the Benedict-Webb-Rubin equation of state is 0.8% for Range 1. For Ranges 2 and 3, the differences were 2.6% and 1.1%.

**Limitations.** Strictly speaking, the procedure in this article should be used only for nonpolar gases and vapors because the compressibility data that have been used to determine the constants are for nonpolar gases and vapors. Of course, most hydrocarbons meet this criterion.

As a practical matter, the procedure of this article can be used for mildly polar gases and vapors. But the error will be larger. Also, the constants for Range 1 should be used only up to the critical point.

For Range 2, the reduced temperature should be between 1.0 and 1.02 and the reduced pressure between 1.0 and 1.5.

For Range 3, the reduced temperature should be between 1.05 and 1.5, and the values of reduced pressure should be between 1.2 and 5.

For applications outside these limits, one just merely defines new ranges and performs the searches as described above.

The computing requirements are modest; 1.9 min of CPU time was required to generate Table 2 using a VAX 11/785.

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# Selective neutralization of overhead crude-unit corrosion by $SO_x$ is identified and controlled

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During the past few years, there have been a few crude-unit overhead systems with good desalting and good corrosion-control programs which have experienced severe corrosion problems.

It was thought that an oxygen-sulfur species was responsible for this corrosion in addition to the principal corrosive agent hydrogen chloride (HCl).[1]

More recently, there has been controversy in the refining industry over the importance of sulfur oxides ($SO_x$) as a major contributor to crude-unit corrosion. Consequently, an extensive research program was undertaken to study the combined corrosive effects of $SO_x$ and HCl. This research led to the development of an effective treatment program.

**Corrosion study.** A survey showed there were several crude units where good corrosion-control programs were utilized, but unacceptably high corrosion rates were observed. The patented overhead corrosion simulator (OCS) shown in Fig. 1 was developed to monitor dew-point corrosion in heat exchangers and condensers.[2] The OCS consists of a baffled water box containing a piping coil. The coil contains 12 corrosion probes which allow collection of corrosion data at 12 temperature zones.

Table 1

### Accumulator SOx results by ion chromatography

| Sample | $Cl^-$, ppm | $SO_3^=$, ppm | $CO_4^=$, ppm | $S_2O_3^=$, ppm |
|---|---|---|---|---|
| Day 1 | 12 | 1 | 5 | 270 |
| Day 2 | 11 | 32 | 2 | 330 |
| Day 3 | 14 | 31 | 9 | 330 |
| Day 4 | 23 | 12 | 7 | 330 |

A thermometer housed in close proximity to the probes provides accurate temperature data at each zone. Cooling is provided by a countercurrent flow of cooling water on the coil external surface. In addition, the coil is designed to allow sampling of the process stream at each temperature zone.

Studies with the OCS showed that peak corrosion activity does not always occur at the dew point, and in many cases, the corrosion is most concentrated at temperatures 10 or more degrees below the dew-point temperature. One correlation with this observation was a higher sulfur content in the crude charge.

The principal corrosive agent in the crude unit overhead equipment is HCl. The HCl is produced by hydrolysis of inorganic salts carried in the crude oil from the desalter.

Magnesium and calcium chlorides are the major sources of HCl.

The HCl vapor itself is not corrosive, but it becomes extremely corrosive when temperatures in the overhead system fall below the dew point of water.

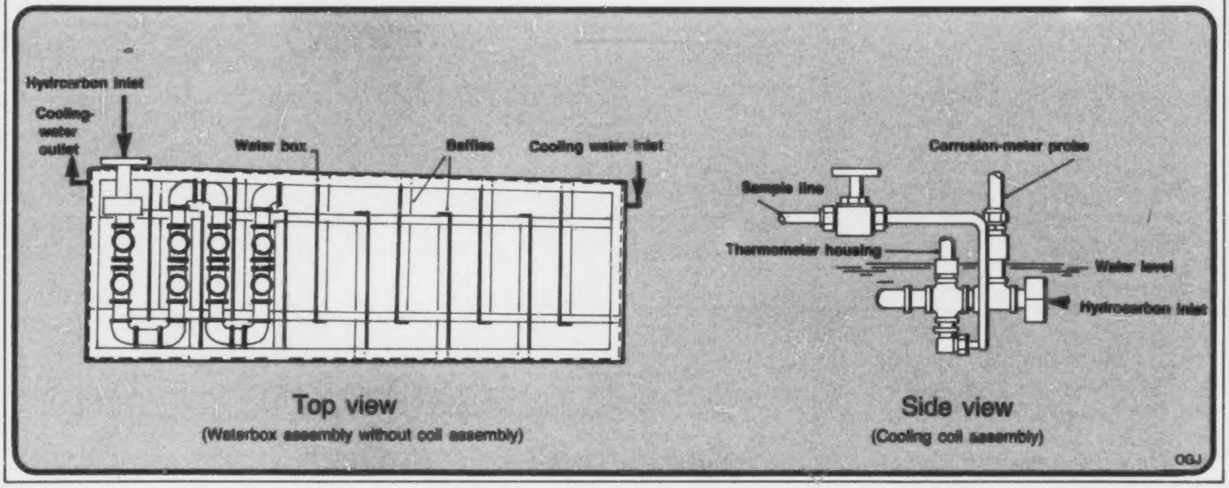
Under these conditions, the HCl dissolves in the liquid aqueous phase to produce hydrochloric acid.

Hydrogen sulfide ($H_2S$) has a significant role in the continuation or acceleration of hydrochloric acid corrosion. $H_2S$ has limited solubility in hot water. However, $H_2S$ accelerates HCl corrosion at the dew point of water by formation of insoluble ferrous sulfide which releases additional HCl.

But increased $H_2S$ production is an

Fig. 1

Overhead-corrosion simulator



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Based on a paper presented at the National Petroleum Refiners Association annual meeting, Los Angeles, Mar. 23-25.

Table 2

## SOx results from OCS samples

| Sample time | Sample point | | OCS location temperature, °F. | Cl⁻, ppm | $SO_3^=$, ppm | $SO_4^=$, ppm |
|---|---|---|---|---|---|---|
| Day 1 | 6 | Vapor | 230 | 6 | 230 | 27 |
| | 6 | Condensate | 230 | 82 | 550 | 6 |
| | 11 | Vapor | 185 | 1 | 230 | 27 |
| | 11 | Condensate | 185 | 120 | 370 | 5 |
| Day 2 | 6 | Vapor | 230 | 6 | 390 | 31 |
| | 6 | Condensate | 230 | 210 | 670 | 6 |
| | 11 | Condensate | 185 | 380 | 390 | 31 |

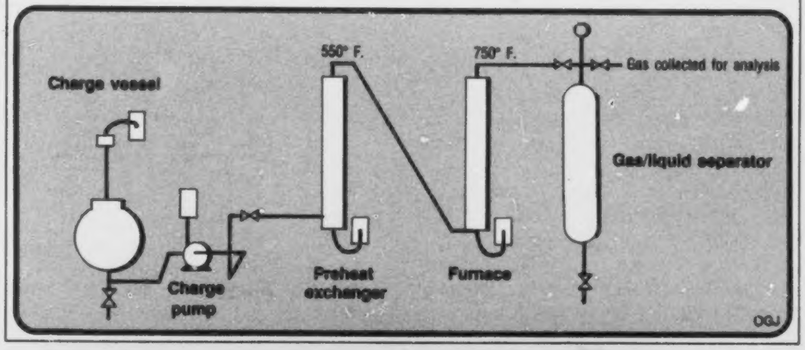
Table 3

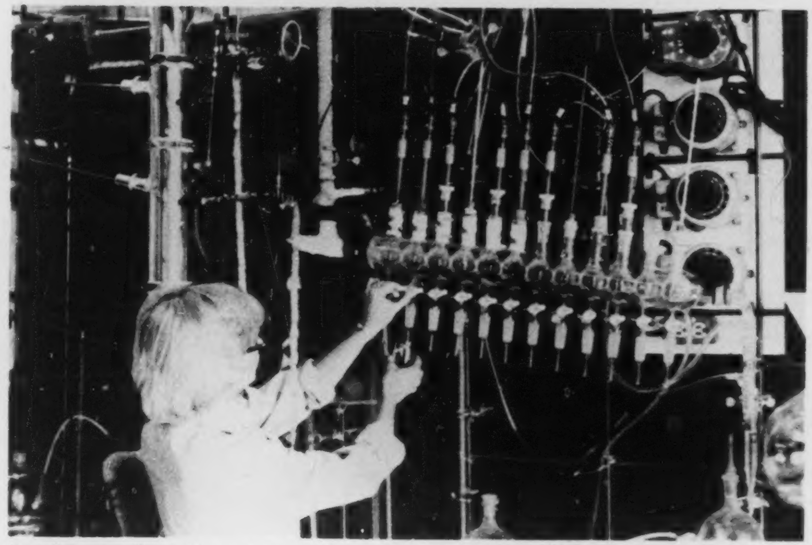
## Furnace simulator SOx results

| Desalter crude sample | $SO_3^=$, ppm | $SO_4^=$, ppm | $S_2O_3^=$, ppm |
|---|---|---|---|
| Crude Blend 1 | 106 | 34 | 310 |
| | 135 | 13 | 370 |
| | 161 | 12 | 250 |
| Crude blend 2 | 135 | 18 | 620 |
| | 35 | 9 | 431 |

Fig. 2

Crude-oil furnace simulator





**Samples are collected** from 12 corrosion probes which allow collection of corrosion data at 12 temperature zones (Fig. 3).

inadequate explanation for the continued corrosion in the units with good corrosion control because increased $H_2S$ would accelerate chloride (dew point) corrosion. One possibility is another acidic species which has a different condensate profile than HCl.

**$SO_X$ identified.** Since it has been postulated that an aggressive species other than chloride was causing corrosion, it then became necessary to identify it. The accumulator water from the same Gulf Coast refinery where the OCS data were obtained was sampled during several days and analyzed. The samples were analyzed by ion chromatography (Table 1).

The chloride concentrations were low in all the samples as were the sulfate levels. The sulfite ($SO_3^=$) level varied from very low (1 ppm) to 32 ppm. The anion in highest concentration was thiosulfate ($S_2O_3^=$) which was more than 300 ppm in nearly all of the samples.

Samples were also taken on several days from the OCS. Samples of condensate and vapor were taken from a hot and a cold location. These data show very high levels of sulfite in all of the samples (Table 2).

**$SO_X$ origin.** Since it had been established that $SO_x$ species were present in the overhead condensing system and accumulator, and that there was a corrosion problem, the research was then directed toward ascertaining the origin of $SO_x$. A crude-unit furnace simulator was developed for this work. The unit schematic diagram is shown in Fig. 2. The objective was to determine if the $SO_x$ was related to the crude slate which was being charged.

In the testing, samples of desalted crude were pumped through a preheater held at an outlet temperature of 550° F. Because this refinery operated with a high crude-furnace outlet temperature, the outlet temperature for the simulator was maintained at 750° F. The crude then entered a heated surge tank.

The vapors from the surge tank were passed through a trapping solution. The experiments were 3 hr in duration. At the conclusion of each experiment, the trapping solution was analyzed by ion chromatography.

The data indicate that changes in the crude slate also change the levels of $SO_x$ species (Table 3). The connection between crude slate and the presence of $SO_x$ and, therefore, overhead corrosion, is also suggested.

**$SO_X$ chemistry.** To better define the origin of the $SO_x$ species, the chemistry of sulfur oxides was reviewed. The objective was to better define what functional groups present in the crude resulted in $SO_x$ generation.

The chemistry of the sulfur oxides is very dependent on pH and is extremely complex. Sulfur dioxide is very soluble in water and yields bisulfite ($HSO_3^-$).

Aqueous solutions of $SO_2$ have long been referred to as sulfurous acid ($H_2SO_3$), but modern physical methods have shown that $H_2SO_3$ is either not present or present in infinitesimal quantities.[3] The following equation best describes the aqueous $SO_2$ chemistry:

Fig. 4

## Neutralization-evaluation unit

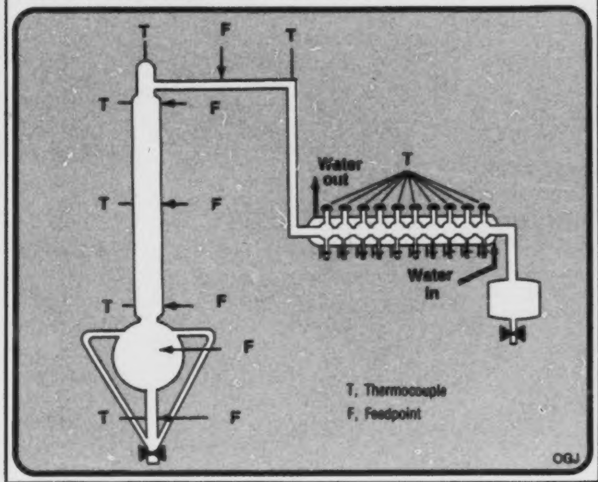
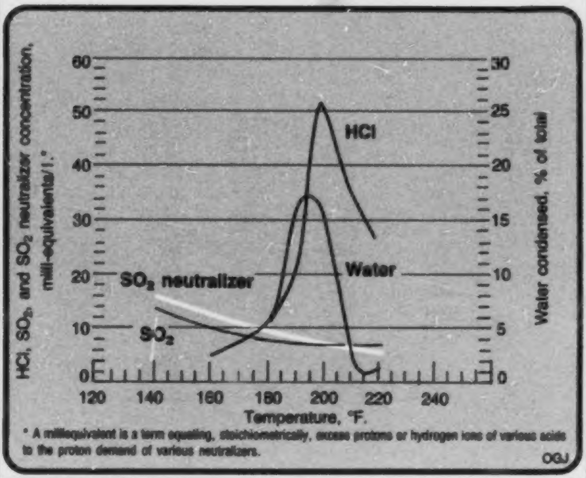

T
F
T
T
F
Water out
T
T
F
Water in
T
F
F
T
F
T, Thermocouple
F, Feedpoint
OGJ

Fig. 5

## Aqueous condensation profiles



* A milliequivalent is a term equaling, stoichiometrically, excess protons or hydrogen ions of various acids to the proton demand of various neutralizers.

$$SO_2 + HO_2 \rightleftarrows HSO_3^- + H^+ \qquad (1)$$

Additionally, since $SO_2$ has a high vapor pressure when over water, which is higher than HCl, the temperature for the bisulfite to form must be below the water dew pont.

Thiosulfuric acid ($H_2S_2O_3$) is unstable at ambient temperatures.

The thiosulfate anion ($S_2O_3^=$) can be generated by reaction of bisulfite and $H_2s$:

$$4HSO_3^- + 2H_2S \rightleftarrows 3S_2O_3^= + 2H^+ + 3H_2O \qquad (2)$$

Thiosulfate has been found to be corrosive to mild steel with the corrosion product being iron sulfide.[4] Thiosulfate can also be generated from free sulfur, which could form from the reaction of $H_2S$ and $SO_2$:

Fig. 6

## Comparative corrosion rates

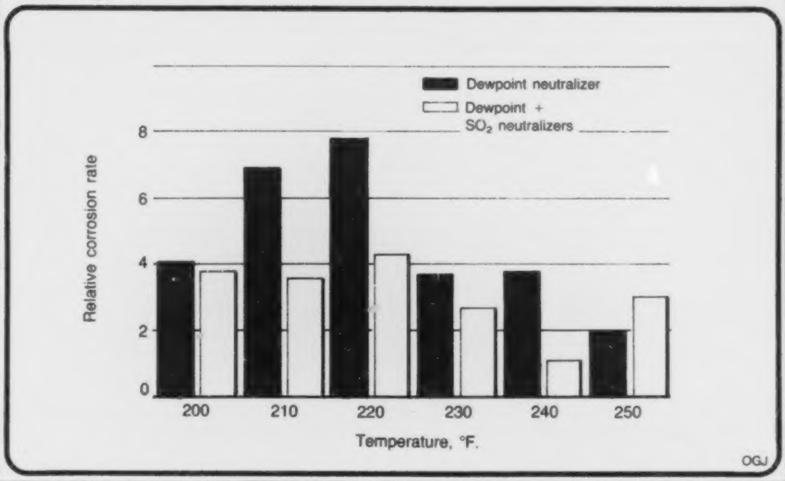


Fig. 7

## Water-collection system

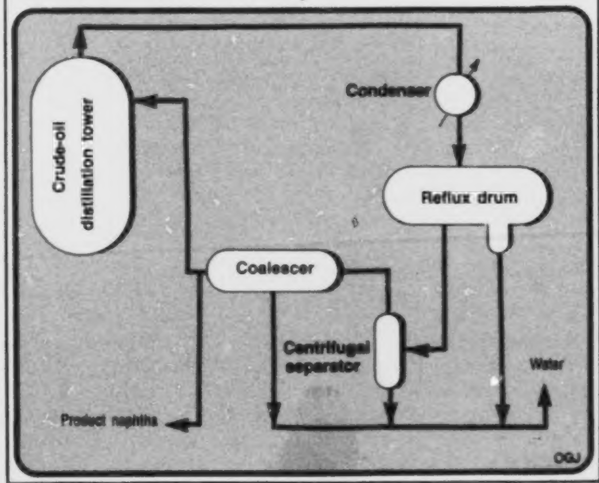
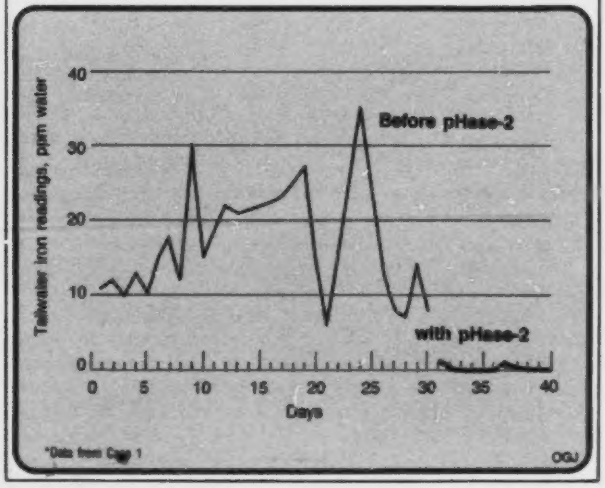

Crude-oil distillation tower
Condenser
Reflux drum
Coalescer
Centrifugal separator
Water
Product naphtha
OGJ

Fig. 8

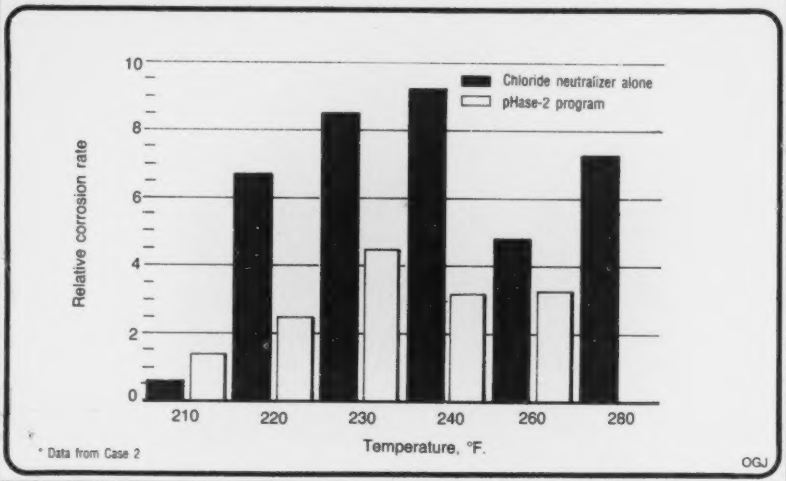
## Iron levels with corrosion control*



*Data from Case 1

Fig. 9

Overall corrosion rate lower with control*



$$2H_2S + SO_2 \rightleftarrows 3S^\circ + 2H_2O \quad (3)$$

$$S^\circ + HSO_3^- \rightleftarrows S_2O_3^= \quad (4)$$

Dithionic acid ($H_2S_3O_6$) is a moderately strong acid. The dithionate could be generated from bisulfite and thiosulfate:

$$4HSO_3^- + S_2O_3^= + 2H^+ \rightleftarrows 2S_3O_6^= + 3H_2O \quad (5)$$

Polythionates ($S_nO_6^=$) are known. The free acids are unstable and decompose rapidly. Tetrathionate ($S_4O_6^=$) can be formed from bisulfite and $H_2S$:

$$3HSO_3^- + H_2S + H^+ \rightleftarrows S_4O_6^= + 3H_2O \quad (6)$$

Sulfate ($SO_4^=$) can be generated by decomposition of thiosulfite in alkyaline solutions:

$$S_2O_3^= \; OH^- \rightleftarrows SH^- + SO_4^= \quad (7)$$

**$SO_2$ neutralizer.** Examination of the $SO_x$ analytical results from the OCS and accumulator and consideration of the $SO_x$ chemistry seemed to indicate that $SO_2$ or bisulfite was the key. The research program, therefore, was directed towards control of corrosion from the absorption of $SO_2$ into water.

The neutralizer evaluation unit (Figs. 3 and 4), was utilized. The specially designed condenser allowed collection of condensate at various temperatures.

Unlike HCl, $SO_2$ is absorbed with increasing concentration in the cooler condensing water, as much as 10 or more degrees below the water dew point.

Using this unit, numerous neutralizer candidates were evaluated for condensation profiles similar to $SO_2$. Fig. 5 depicts the condensation profile for HCl, $SO_2$, and a $SO_2$ neutralizer.

The water and HCl have similar profiles. However, the concentration of $SO_2$ in the water increases at temperatures below that of HCl.

Additionally, the profile for the $SO_2$ neutralizer is identical to that of $SO_2$. Therefore, the neutralizer will abate corrosion by being present where $SO_2$ is condensing to react with the resultant $SO_x$ species.

**Neutralizer evaluated.** A neutralizer with a condensation profile identical to $SO_2$ had been developed. However, it was now necessary to determine if this neutralizer could decrease the corrosion due to $SO_x$.

The $SO_2$ neutralizer was tested in the OCS on a crude-unit overhead system (Fig. 6). The data show that the performance of the dew point chloride neutralizer was improved by addition of an $SO_2$-selective neutralizer.

The $SO_2$ was causing corrosion 15-20° F. below the 235° F. dew point. When compared with treatment by a dew point chloride neutralizer alone, the combination of chloride and $SO_2$ neutralizers resulted in a corrosion rate reduction of 50% at the temperature of highest corrosion. The average corrosion reduction for all temperatures was 29%.

**Strong acid test.** A new corrosion-control concept was developed using the selective neutralizer approach. However, in order to feed selective neutralizers, it was necessary to determine the concentrations of HCl and $SO_x$ so that the proper quantities of each neutralizer could be added to the overhead system.

A test for strong acids in the accumulator water was developed which allows the appropriate type of neutralizers necessary for corrosion control to be determined.

First, the accumulator water is measured for total required neutralizer, then chloride-equivalent measurements are subtracted from the original test measurements to arrive at the proper requirement for each neutralizer. The resulting water pH then becomes the new target pH for that individual system and feedstock.

The corrosion control program adjusts pH with selective equivalents, using two neutralizers. Called pHase-2, the program was introduced in March 1985.

**Case histories.** In a major refinery on the West Coast, high iron levels were continually observed in the tailwaters from a sour-crude unit. Although the refiner increased the rate of chloride neutralizer and filmer, this did not sufficiently reduce the iron level.

Water analysis for iron is commonly used but may not always be a good measure of corrosion activity. The iron levels may not be reflective of corrosion rates because the iron is converted to iron sulfide which is insoluble in both water and hydrocarbon.

The particulate iron sulfide may tend to float at the naphtha/water interface. Additionally, it is possible for the filming inhibitor to cause the iron sulfide particles to preferentially follow the naphtha flow path rather than the water flow path. When this happens, the concentration of iron in the water may be misleading.

In the case of this refiner, water was taken from three different sources: the reflux drum, the naphtha centrifugal separator, and the naphtha coalescer (Fig. 7).

The centrifugal separator and coalescer both remove particulate and water from the naphtha; therefore, the corrosion products flow with the water. These water streams were then combined to get an adequate sample of water for iron determination.

The corrosion-control program was implemented on this unit, and in a few days, the iron levels dropped from 20 ppm to 0.2 ppm (Fig. 8). The iron levels remained low until the original corrosion control program, using only a chloride neutralizer, was reinstituted to verify the previous results. When the switch was made, the iron levels began to increase once again.

In a second major refinery on the West Coast, an OCS was in parallel to the overhead system. The unit processes sour crude. The OCS was monitored to determine the efficiency of the program.

The corrosion-control program was instituted for an evaluation. The strong-acid test was used to determine chemical requirements, and the corrosion rates were monitored.

After about 40 days, the original chloride-only neutralizer program was

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reinstituted to determine the benefit of the program. The data from the evaluation are shown in Fig. 9. The corrosion rates with the program are lower overall than that with only chloride neutralization. Additionally, there was a dramatic decrease in the 210-215° F. region which is about 20° F. below the water dew point.

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# Method provides accurate calculation of HD-5 propane densities

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An accurate means of determining liquid densities can reduce the error in metering propane flows, to roughly 0.2% from over 1%. The COSTALD method provides the needed accuracy.

Roughly 870,000 bbl of propane changes hands daily, according to U. S. Department of Energy statistics.[1] A major portion of this propane is called HD-5, which is an important heating fuel.

Specifications limit the butane content in HD-5 to 2.5 vol % ( ≈ 2.1 mole %) or less and the ethane content to a level such that the vapor pressure of the mixture does not exceed 208 psig at 100° F.[2] This limits the maximum ethane content to about 8 vol % or mole %.

Years ago, ethane recovery methods were such that little ethane was included in HD-5 propane. However, recovery methods have improved and relative values for ethane and propane have shifted. These factors make it both feasible and economically attractive to maximize the ethane content.

Having the maximum allowable ethane content affects most of the mixture's properties only slightly and provides benefits to both the producer and consumer. However, producers have found that they sometimes experience apparent inventory shortages with the higher ethane levels. These apparent shortages may be caused by the method used to calculate HD-5 densities.

**Density calculation.** For metering purposes, the typical reference condition is the hypothetical liquid at 60° F. and 14.7 psia. Converting from volumetric measurements to mass measurement requires knowing the density.

Typically, the density is computed by a method which uses the measured composition. The simplest and most obvious method is to assume that the mixture is ideal; this implies that the molar volume of the mixture ($V_m$) is a weighted average of the molar volumes of the pure components:

$$V_m = 84.50\, x_{C_2} + 87.06\, x_{C_3} + 103.36\, x_{iC_4} + 99.62\, x_{nC_4} \qquad (1)$$

The x values denote the mole fraction of each component. The molar volumes are computed from GPA Standard 2145-85.[3] The units are cc/mole.

The GPA standard tabulates specific

Fig. 1

Density deviation*

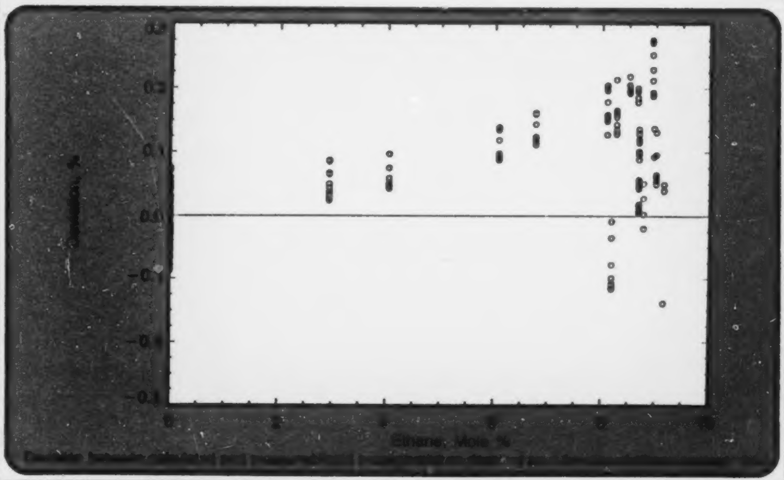

Table 1

## Coefficients for COSTALD correlation

| | j | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| a | −1.52816 | 1.43907 | −0.81446 | 0.190454 |
| b | −0.296123 | 0.386914 | −0.0427258 | −0.0480645 |
| c | −9.070217 | 62.45326 | −135.1102 | |

Table 2

## Pure fluid properties

| | Methane | Ethane | Propane | Butane | i-Butane |
|---|---|---|---|---|---|
| TC(K) | 190.59 | 305.43 | 369.83 | 425.19 | 408.15 |
| ω | 0.0074 | 0.0983 | 0.1532 | 0.2008 | 0.1825 |
| V* | 0.0994 | 0.1458 | 0.2001 | 0.2544 | 0.2568 |
| $d_1$ | 4.251053E+1 | 5.777045E+1 | 7.840671E+1 | 8.498264E+1 | 8.272078E+1 |
| $d_2$ | −1.473223E+3 | −2.844333E+3 | −4.044426E+3 | −4.960500E+3 | −4.672691E+3 |
| $d_3$ | 2.523658E−2 | 1.802736E−2 | 2.044045E−2 | 1.822010E−2 | 1.862912E−2 |
| $d_4$ | −6.814500E+0 | −8.755501E+0 | −1.205760E+1 | −1.279500E+1 | −1.252500E+1 |

Table 3

## Density

| Composition, mole fraction | | | | Density, g/cc | | | | |
|---|---|---|---|---|---|---|---|---|
| $C_2$ | $C_3$ | $iC_4$ | $nC_4$ | Measured | Ideal mixing | % Deviation | COSTALD | % Deviation |
| 0.0000 | 0.9893 | 0.0092 | 0.0015 | 0.5078 | 0.5073 | −0.10 | 0.5077 | −0.03 |
| 0.0293 | 0.9603 | 0.0089 | 0.0015 | 0.5048 | 0.5030 | −0.35 | 0.5049 | 0.03 |
| 0.0403 | 0.9494 | 0.0088 | 0.0015 | 0.5038 | 0.5013 | −0.50 | 0.5040 | 0.04 |
| 0.0607 | 0.9293 | 0.0086 | 0.0014 | 0.5017 | 0.4983 | −0.68 | 0.5021 | 0.09 |
| 0.0675 | 0.9225 | 0.0086 | 0.0014 | 0.5010 | 0.4973 | −0.73 | 0.5015 | 0.12 |
| 0.0808 | 0.9094 | 0.0084 | 0.0014 | 0.4996 | 0.4954 | −0.84 | 0.5002 | 0.13 |
| 0.0000 | 0.9769 | 0.0231 | 0.0000 | 0.5090 | 0.5080 | −0.20 | 0.5085 | −0.09 |
| 0.0893 | 0.8896 | 0.0211 | 0.0000 | 0.5000 | 0.4949 | −1.02 | 0.5010 | 0.19 |
| 0.0876 | 0.9123 | 0.0000 | 0.0000 | 0.5001 | 0.4937 | −1.28 | 0.5000 | −0.02 |

gravities of the pure fluids. These values are converted to absolute densities using 0.99901 g/cc as the density of water at 60° F. and 14.7 psia.[4]

To obtain the density (ρ) in g/cu m:

$$\rho = mw/V_m \qquad (2)$$

where mw is the calculated average molecular weight:

$$mw = 30.070\ x_{C_2} + 44.097\ x_{C_3} + 58.123\ (x_{iC_4} + x_{nC_4}) \qquad (3)$$

The molecular weights for each component are also from the GPA Standard 2145-85. A more complex method, but tractable on a hand calculator for computing the molar volume and then the density, is the COSTALD method. The original version of this correlation applied only to saturated liquids.[5] But it was later extended to the compressed liquid region.[6]

The method will be described briefly here. The original work should be examined to obtain a more fundamental understanding of the methods. Saturated liquid volumes (Vs) are calculated using:

$$V_s/V^* = V_R[1 - {}^{(o)}\ \omega_{SRK}\ V_R^{(\delta)}] \qquad (4)$$

$$V_R^{(o)} = 1 + \sum_{j=1}^{4} a_j\,(1 - T_R)^{j/3} \qquad (5)$$

$$V_R^{(\delta)} = [\sum_{j=1}^{4} b_j\ T_R^{(j-1)}]/(T_R - 1.00001) \qquad (6)$$

$T_R$ is the reduced temperature. Table 1 lists the values of $a_j$ and $b_j$. Values of the pure fluid properties $V^*$, $\omega_{SRK}$, and $T_c$ are listed in Table 2.

The method is extended to mixtures by using the following mixing rules to calculate $V^*_m$, $\omega_m$, and $T_{cm}$ for mixtures. These values replace their pure fluid counterparts in Equations 4 through 6:

$$T_{cm} = [\sum_i \sum_j x_i\ x_j\ V^*_{ij}\ T_{cij}]/V^*_m \qquad (7)$$

$$V^*_m = \tfrac{1}{4}[\sum_i x_i\ V^*_i + 3(\sum_i x_i\ V_i^{*2/3})(\sum_i x_i\ V^{*1/3})] \qquad (8)$$

$$V^*_{ij}\ T_{cij} = V^*_i\ T_{ci}\ (V^*_j T_{cj})^{1/2} \qquad (9)$$

$$\omega_m = \sum_i x_i\ \omega_{SRKi}$$

The method is extended to pure compressed liquid by using:

$$V/V_s = 1 - C\ \ln[(B + P)/(B + P_s)] \qquad (10)$$

$$B/P_c = -1 + \sum_{j=1}^{4} c_j\,(1 - T_R)^{j/3} \qquad (11)$$

$$C = 0.0861488 + 0.034483\ \omega_{SRK} \qquad (12)$$

The value of $c_4$ is given by:

$$\ln c_4 = 4.79594 + 0.250047\ \omega_{SRK} + 1.14188\ \omega^2_{SRK} \qquad (13)$$

Table 1 lists the remaining $c_j$. The critical pressure ($P_c$) of the pure components is given in Table 2. The table also lists coefficients (d) of the pure fluid vapor pressure equation:

$$\ln P_s = d_1 + d_2/T + d_3 T + d_4 \ln T \qquad (14)$$

To extend this calculation to mixtures ($P_{cm}$) where R is the gas constant:

$$P_{CM} = (Z_{CM}\ RT_{CM})/V^*_M \qquad (15)$$

$$Z_{CM} = 0.291 - 0.080\ \omega_{SRK} \qquad (16)$$

The mixture vapor pressure ($P_{SM}$) is the product of $P_{RM}$ and $P_{CM}$, where:

$$\log P_{RM} = P^{(0)}_{RM} + \omega_{SRK}\ P^{(1)}_{RM} \qquad (17)$$

$$P_{RM}^{(o)} = 5.8031817 \log T_{RM} + 0.07608141\ \alpha \tag{18}$$

$$P_{RM}^{(1)} = 4.86601\ \beta \tag{19}$$

$$\alpha = 35.0 - 36.0/T_{RM} - 96.736 \log T_{RM} + T_{RM}^{6} \tag{20}$$

$$\beta = \log T_{RM} + 0.03721754\ \alpha \tag{21}$$

Once the liquid volume is computed, the density is calculated using Equations 2 and 3.

**Density data.** In spite of the large quantities of HD-5 propane bought and sold, there are few density data in the open literature on liquid propane mixtures containing low levels of ethane, isobutane, and n-butane.

There are five sets of density data for the propane-normal butane system which are accurate to 0.5% or better.[7,8,9,10,11] Only Kahare[8] reports density data for the propane-isobutane system.

For the ethane-propane system, there are four sets of data.[7,8,11,12] There are two sets of data for multicomponent systems.[10,11]

However, none of these data have compositions comparable to those found in HD-5 propane.

To obtain density data on mixtures typical of HD-5 propane, two series of density measurements were made. In the first set, densities were measured on propane mixtures containing 2.5 mole % isobutane and/or 8 mole % ethane.

Data were taken at 60, 105, 115, and 130° F., and at pressures to 600 psia.

In the second set, densities were obtained on a propane mixture containing roughly 0.8 mole % isobutane and 0.2 mole % n-butane, with varying amounts of ethane. The purpose of these measurements was to look at the effect of ethane content on density for one typical propane mixture. All of these data were obtained at 60° F. and at pressures to 400 psia.

The measurements[9,10] were made using a vibrating tube densimeter submerged in a bath and held constant to ±0.1° F. or better. The temperature was determined to better than 0.1° F. using a platinum resistance thermometer. Pressure measurements were made using a differential pressure gauge connected to a quartz bourdon tube gauge. By calibrating the gauge against air and oil deadweight gauges, pressure readings were obtained with an accuracy of better than 0.5 psi.

Pure argon and propane were used to calibrate the densitometer. Densities were calculated for these fluids as a function of temperature and pressure using a 32-term equation of state with the coefficients listed by Parrish.[9]

## The author. . .

**Parrish**

W.R. Parrish is a research associate in Phillips Petroleum Co.'s research and developemnt department, where he has worked for 7 years. He and his group are responsible for obtaining, evaluating, and correlating thermophysical properties of fluids needed for the design and operation of refining and petrochemical processes.

Prior to this, he worked as a chemical engineer at the National Bureau of Standards in Boulder, Colo. Parrish holds a BChE degree from Georgia Tech, and MS and PhD degrees in chemical engineering from the University of California, Berkeley. He is a member of the Enthalpy Research Committee of the Gas Processors Association and a member of AIChE, ACS, and Sigma Xi.

Mixture compositions were prepared by weight. Research grade components were used. The propane and butanes were put through a purification procedure to eliminate any residual air.

An error analysis of the experiment shows that the measured densities have an uncertainty of 0.2%. This is because the density of the calibration fluids is known only to 0.2%. Based on uncertainties in weighing, the mixture compositions have an estimated total uncertainty of less than 0.02 mole %.

This project involved studying 17 mixtures and 180 data points. A table of the data is available upon request from the author.

**Density comparison.** A comparison between measured densities and densities computed using COSTALD indicates an average error of 0.08%, with a bias of +0.06%. The deviation is defined as the calculated density minus the measured density, all divided by the measured density.

The maximum error was 0.28%; all errors of greater than 0.2% occurred in mixtures containing more than 8 mole % ethane. The deviation tends to increase with increasing ethane content (Fig. 1). These deviations are typical of those reported for COSTALD in other liquid mixtures of ethane, propane, and butanes.[13] These comparisons show that COSTALD is sufficiently accurate for use in custody transfer and for purposes of internal inventory. As mentioned earlier, most metering operations are based on saturated liquid densities. The density measurement method used here only measures densities reliably if the mixture is in a single phase.

However, density measurements were made at pressures within 10 psi of the mixture bubble point and these values are used for the comparison. Table 3 presents a comparison of the densities calculated using the ideal mixing method and those calculated with COSTALD with the measured values very near the bubble point.

These results clearly show that at the higher ethane concentrations, the ideal mixture approach is too inaccurate for custody transfer calculations. The deviation is a linear function of ethane content for the mixture containing both iso and normal butanes. Unfortunately, we cannot generalize this relationship to all HD-5 mixtures because the slope also depends upon the butane content. By comparison, Table 3 shows the densities calculated using COSTALD to be within 0.2% for all of the mixtures. There is an increase in the deviation with increasing ethane content but the maximum deviation is still within the uncertainty of the measurements.

Therefore, COSTALD provides the needed accuracy without being too complex for most field applications.

**Acknowledgments.** This work was partially supported by the Northern Gas Products Co. All measurements were performed by J.L. Durm.

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# Nomographs estimate floating-roof-tank

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An estimate of the average evaporation loss for external floating-roof tanks can be quickly and easily determined using the nomographs presented in Figs. 1-3.

The nomographs relate tank diameter, type of seal (see box), vapor pressure of the stored product, and wind velocity.

The nomographs are based on guidelines presented in API publication 2517, "Evaporation loss from Floating-Roof-Tanks."

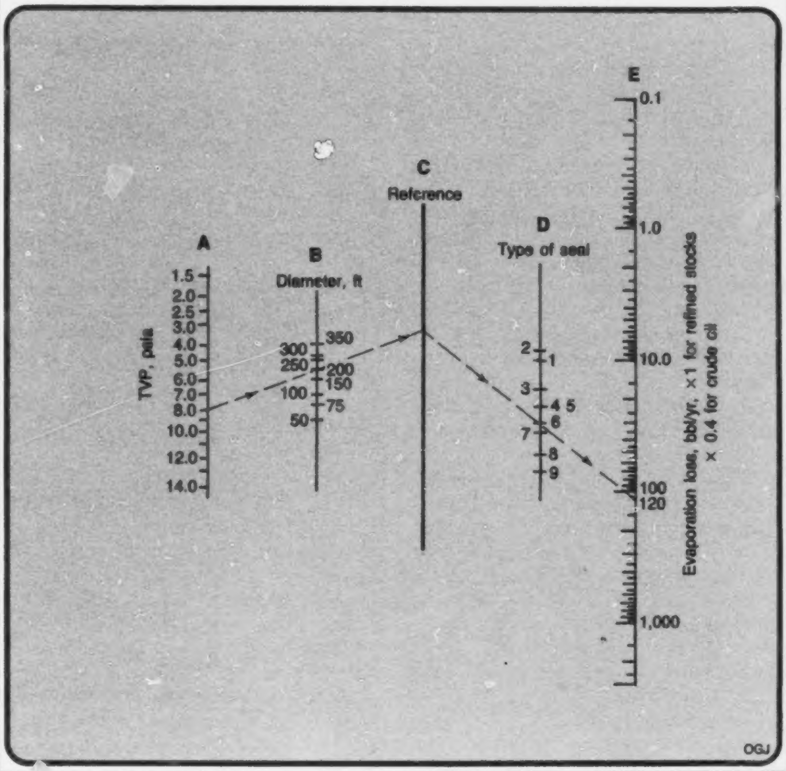
The evaporation loss determined from the nomographs assumes insignificant withdrawal loss — loss associated with the movement of product in and out of the tank — and represents average standing storage loss only.

For crude oil, the determined evaporation loss, read on axis E, must be multiplied by a factor of 0.4. For refined stocks, the evaporation loss is determined directly from axis E without a factor.

Average evaporation loss can be estimated using the nomographs for tank diameters ranging from 50 ft to 350 ft.

Fig. 1

Evaporation loss at 5-mph wind velocity



## Type of seal*

1. Liquid-mounted, resilient-filled seal with rim-mounted secondary
2. Mechanical shoe seal with rim-mounted secondary
3. Liquid-mounted resilient-filled seal with weather shield
4. Liquid-mounted, resilient-filled seal, primary seal only
5. Mechanical shoe seal with shoe-mounted secondary
6. Mechanical shoe seal, primary seal only
7. Vapor-mounted, resilient-filled seal with rim-mounted secondary
8. Vapor-mounted, resilient-filled seal with weather shield
9. Vapor-mounted, resilient-filled seal with primary seal only

* Use for value of Axis D; from API 2517.

True vapor pressures range from 1.5 to 14 psia.

The nomographs cover the most commonly used tank seals.

Three wind velocity conditions are covered and are: 5 mph (Fig. 1), 10 mph (Fig. 2), and 15 mph (Fig. 3).

The evaporation loss determined from the nomographs can be used for economic evaluation of seal conversion and for reconciliation of refinery/terminal oil losses.

Use of the nomographs is illustrated by the following example:

Determine the evaporation loss for an external floating-roof tank, containing crude oil, that is 200 ft in diameter with a mechanical shoe seal (primary seal only), at a wind velocity of 10 mph.

The true vapor pressure of the crude oil is 8 psia.

### Solution:

1. Use Fig. 2 for the specified wind velocity of 10 mph.
2. Locate true vapor pressure (TVP) of 8 psia on axis A.
3. Locate tank diameter of 200 ft on

# evaporation

## The author. . .

**Sivaraman**

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axis B.

4. Connect the two points (on axis A and axis B) and extend it to intersect the reference axis C.

5. Locate the type of seal (number 6 for mechanical shoe seal with primary seal only) on axis D.

6. Join the point of intersection on the reference axis C and point (6) on the seal axis D and extend it to intersect the evaporation axis E.

Read the evaporation loss (Fig. 2) in bbl/yr (450 for the specified conditions) and multiply it by product factor of 0.4 for crude. The average evaporation loss for this example is 180 bbl/yr.

The same example is shown on Figs. 1 and 3 for different wind velocities.

**Summary.** Nomographs are presented that estimate the evaporation loss from external floating-roof tanks using tank diameter, type of seal, product vapor pressure, and wind velocity.

**Reference**

API Publication 2517, "Evaporation Loss from External Floating-Roof Tanks."

Fig. 2

Evaporation loss at 10-mph wind velocity

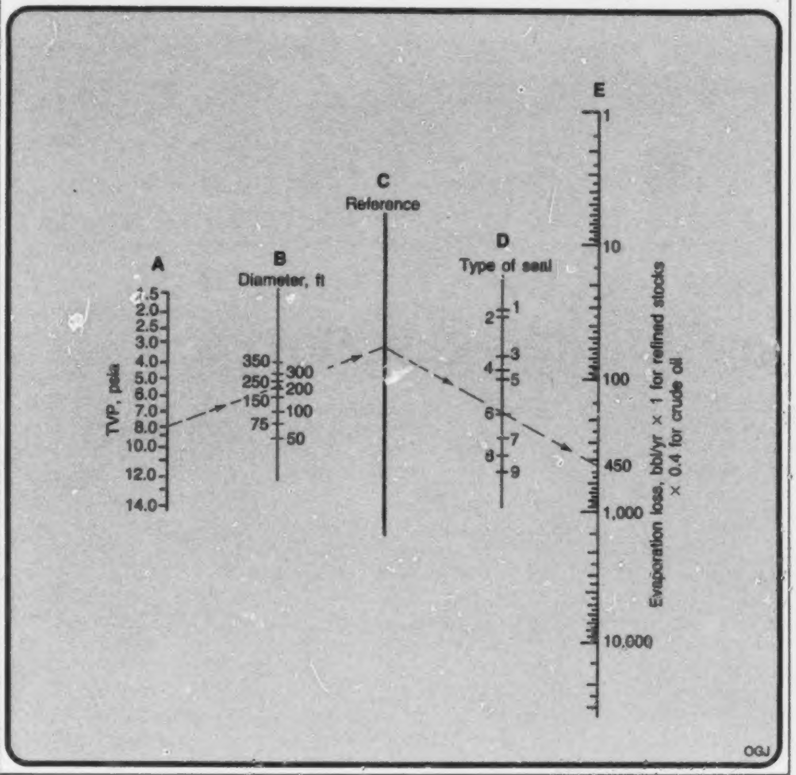
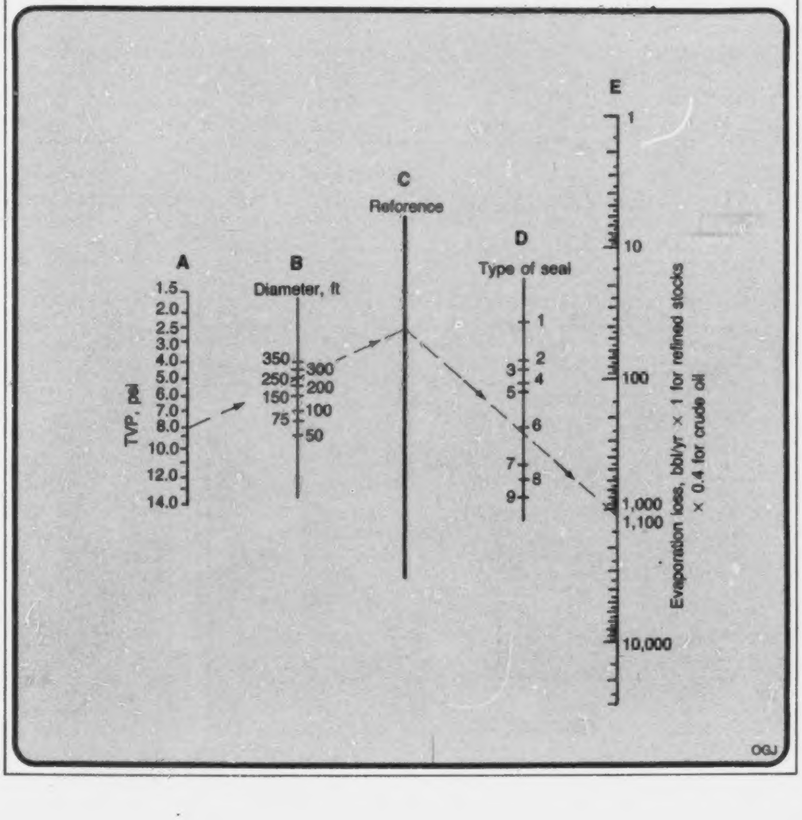


Fig. 3

Evaporation loss at 15-mph wind velocity



# New catalyst permits cut in COS tail-gas emissions

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Carbonyl sulfide emissions in sulfur-recovery-plant tail gas can be reduced to 1 to 2 ppm by using a highly selective COS hydrolysis catalyst in tandem with a CoMo hydrogenation catalyst.

In petroleum refineries or gas plants processing, respectively high-sulfur crudes or natural gas, sulfur will be present in the off gases in the form of $SO_2$, $H_2S$, $CS_2$, COS, and elemental sulfur. In order to efficiently remove sulfur from such a stream, these compounds must be converted to $H_2S$ by either hydrogenation ($SO_2$, $S_n$) or hydrolysis (COS, $CO_2$).

This is typically accomplished in the reactor section of a tail gas cleanup (TGCU) unit over a CoMo catalyst. The $H_2S$ is then removed by scrubbing.

Removal of COS is particularly difficult in these units because the thermodynamics for COS hydrolysis are more favorable than those for COS hydrogenation, and COS is very difficult to remove by conventional scrubbing processes.

But use of a new highly selective catalyst permits reduction of COS to considerably less than equilibrium COS values exit the CoMo reactor at normal operating conditions.

The results of laboratory studies and equilibrium calculations for two different hydrogenation/hydrolysis configurations will be presented and compared to those for a single reactor (CoMo only) system.

**Tail gas processes.** Concern over the ecological problems caused by acid rain has led to the advent of increasingly stringent regulations regarding sulfur emissions to the atmosphere in the tailgas from Claus plants (Fig. 1). Increases in the refining of sour crude oil, the processing of sour natural gas, and the use of higher-sulfur-content coal for electricity generation, or in partial oxidation processes for syn gas generation, have helped necessitate the development of a group of processes that when operated in conjunction with a Claus unit improve the sulfur recovery levels attainable with Claus-based units (typically 95-97%) to levels in excess of 99.9%.

The most efficient of these tail gas cleanup (TGCU) processes are the so-called "wet scrubbing processes" that rely on the conversion, by either hydrogenation or hydrolysis, of all sulfur-containing compounds in the gas exit the Claus unit to $H_2S$.[1]

This hydrogenation/hydrolysis step is accomplished in one reactor over a CoMo catalyst (for example, UCI C29-2-03) prior to removal of the $H_2S$ by either reaction or absorption in the

Table 1

## Typical tail gas composition

| Component | Inlet | Exit C29 |
|---|---|---|
| | (moles/100 | moles wet feed) |
| $H_2S$ | 0.789 | 1.462 |
| $CO_2$ | 7.788 | 8.555 |
| $SO_2$ | 0.395 | — |
| COS | 0.051 | (12.6 ppm vol, dry) |
| $CS_2$ | 0.023 | — |
| $S_n$ | 0.181 | — |
| $N_2$ | 54.940 | 54.940 |
| CO | 0.740 | 0.047 |
| $H_2$ | 3.668* | 2.995 |
| Dry total | 68.575 | 67.999 |
| $H_2O$ | 34.157 | 34.157 |
| Wet total | 102.732 | 102.156 |

*Actual $H_2$ exit Claus unit is 0.936; twice the stoichiometric $H_2$ needed to completely hydrogenate the $SO_2$ and $S_n$ was added.

Fig. 1

## Typical Claus unit for sulfur recovery

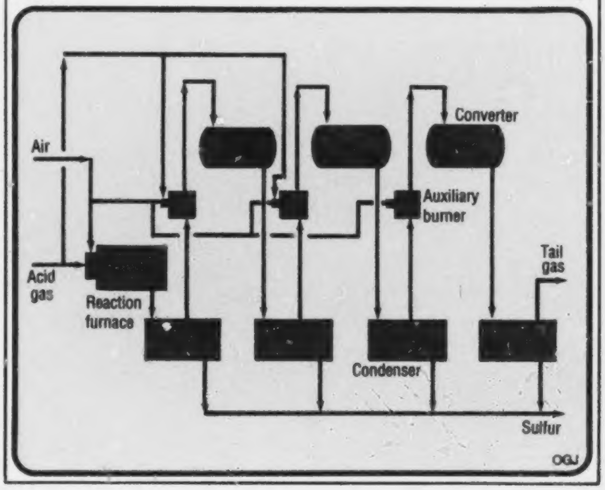

Fig. 2

## Hydrogenation/hydrolysis for TGCU

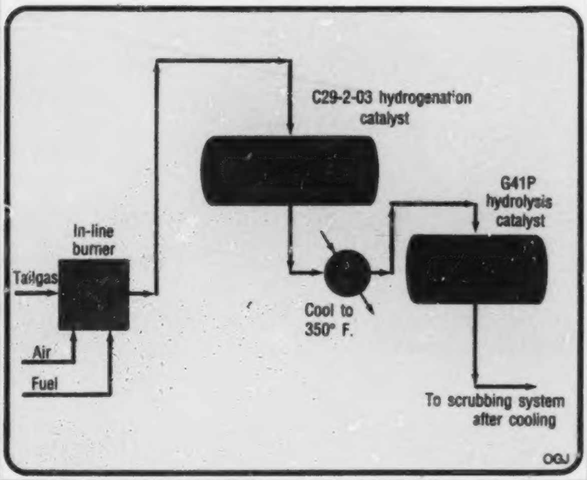

Table 2

## Catalyst evaluation for tail gas hydrogenation

| **Test conditions:** | |
|---|---|
| Temperature, °F. | 500, 550, 575, and 625 |
| Pressure, psig | 5-10 |
| Wet gas space velocity, v/v/hr | 2,000 |
| S/G | 0.45 |
| Feed gas, mole % | |
| CO | 0.56 |
| $CO_2$ | 7.50 |
| $H_2$ | 5.20-6.30 |
| $H_2O$ | 33.00 |
| $N_2$ | balance |

| | | Dry gas composition, ppm | | | |
|---|---|---|---|---|---|
| | | COS | $CS_2$ | $SO_2$ | $H_2S$ |
| 500° F. | | | | | |
| Inlet: | | 2,760 | 776 | 10,153 | 21,666 |
| Exit gas: | C25-2-02 | 562 | 49 | 372 | 23,208 |
| | C29-2-03 | 417 | 27 | 155 | 24,479 |
| 550° F. | | | | | |
| Inlet: | | 2,498 | 728 | 9,463 | 19,696 |
| Exit gas: | C25-2-02 | 476 | 52 | 33 | 22,509 |
| | C29-2-03 | 231 | 30 | 27 | 21,589 |
| 575° F. | | | | | |
| Inlet: | | 2,368 | 538 | 9,077 | 17,469 |
| Exit gas: | C25-2-02 | 373 | 38 | 76 | 22,319 |
| | C29-2-03 | 218 | 36 | 21 | 21,726 |
| 625° F. | | | | | |
| Inlet: | | 1,109 | 491 | 9,151 | 17,028 |
| Exit gas: | C25-2-02 | 118 | 6 | 17 | 20,824 |
| | C29-2-03 | 96 | 2 | 5 | 19,221 |

cases of the Scot process developed by the royal Dutch Shell laboratories in The Netherlands[2] and the Beavon/Stretford process developed by the Ralph M. Parsons Co. and Unocal.[3]

Two newer versions of the Scot process have been developed.

Exxon has introduced a process that includes the use of a highly selective solvent, Flexsorb S.E., to remove $H_2S$ from the gas exit the CoMo reactor.[1] Union Carbide and Ford, Bacon & Davis have combined efforts to develop the Sulften process that utilizes Ucarsol, a solvent capable of removing $H_2S$ to less than 10 ppm vol.[4]

Primarily, these two processes offer improvements in the Scot process by improving the $H_2S$ removal step (for example, some of the newer solvents selectively remove $H_2S$ and are not as affected by $CO_2$ in the stream).

Still, emission regulations are written to cover not only $SO_2$ and $H_2S$ levels but also include a total sulfur specification. These specs, when considered with the fact that carbonyl sulfide can have adverse effects on scrubbing operations for $H_2S$ removal and is itself very difficult to remove by scrubbing,[5] make the removal of COS by hydrolysis prior to the scrubbing step an attractive addition to TGCU designs.

**Hydrogenation/hydrolysis.** Carbonyl sulfide (COS) and carbon disulfide ($CS_2$) are formed in the combustion step of Claus units where hydrocarbons and/or carbon oxides are present in the stream. The inlet stream to the Claus reactor will then contain sulfur as $H_2S$, $SO_2$, COS, $CS_2$, and elemental sulfur ($S_n$).

The primary reaction in the Claus unit (after the initial combustion of a portion of the $H_2S$ to $SO_2$) is

$$2\ H_2S + SO_2 \rightleftharpoons 2\ H_2O + 3/n\ S_n + \text{Heat}$$

Due to the presence of so many sulfur-containing species and other gases, all the reactions taking place in a Claus unit are too numerous to mention.[6] The net result is Claus off gas going to the CoMo reactor (after $S_n$ removal and heating) that contains all of the sulfur compounds mentioned above and significant amounts of water.

In the Scot and Beavon processes, two types of reactions over the CoMo catalyst are involved in the conversion of these compounds to $H_2S$:

**Hydrolysis**

$$COS + H_2O \rightleftharpoons H_2S + CO_2 \tag{1}$$

$$CS_2 + 2H_2O \rightleftharpoons 2H_2S + CO_2 \tag{2}$$

**Hydrogenation**

$$SO_2 + 3H_2 \rightleftharpoons H_2S + 2H_2O \tag{3}$$

$$S_n + nH_2 \rightleftharpoons nH_2S \tag{4}$$

The hydrogen needed for Reactions 3 and 4 can usually be added (in excess to ensure complete hydrogenation) from an external source in refinery operations. Natural gas operations that do not have ready access to an external $H_2$ supply rely on substoichiometric combustion of natural gas in the preheating section between the Claus unit and the CoMo bed to provide the needed $H_2$.

Typically, the CoMo reactor is operated at an inlet temperature between 575 and 660° F. which, besides keeping the elemental sulfur from condensing and fouling the catalyst, strongly favors higher rates for hydrogenation Reactions 3 and 4. Of course, there is also a significant temperature rise resulting from the heat generated in Reactions 3 and 4. Unfortunately, hydrolysis Reaction 1 is favored by lower temperatures. The hydrogenation of COS, i.e.

$$COS + H_2 \rightleftharpoons CO + H_2S$$

is much less favorable than Reaction 1, even at 700 °F.[5]

There is also the drawback of forming more COS over a CoMo at the high $CO_2$ levels often seen in this application by the reverse of Reaction 1. Indications are that if COS is to be removed effectively in TGCU processes, a separate selective COS hydrolysis catalyst should be installed in the system and operated at temperatures considerably lower than those of the CoMo hydrogenation reactor.

**Hydrolysis catalyst.** COS hydrolysis catalysts have been developed and reported elsewhere. Some are designed for use as sulfur-resistant shift catalysts,[7] while others are attractive only if preceded by partial extraction of $H_2S$.[5] It is also possible to use a catalyst in the Claus reactor itself specifically formulated to achieve lower COS levels in the tail gas.[8] The UCC/Ford, Bacon & Davis Sulften system includes a COS hydrolysis catalyst in front of the CoMo reactor.[4]

However, because the gas exiting the CoMo reactor in a TGCU unit has to be cooled to achieve effective scrubbing of the $H_2S$, it would seem logical to:

- Cool to a temperature where COS hydrolysis is favorable thermodynamically (being careful to maintain a temperature sufficient enough to avoid condensation of elemental sulfur).
- Remove the COS to the lowest possible levels.
- Then scrub the $H_2S$.

Use of UCI G41P (a promoted Cr/$Al_2O_3$ catalyst) in this scheme (see Fig. 2) at 350° F. should allow removal of COS to levels of 1-2 ppm, which in turn eliminates any negative effects COS might have on the $H_2S$ scrubbing operation. This arrangement would also eliminate any problems in the COS hydrolysis reaction caused by the presence of $SO_2$.

Before laboratory tests were begun, a brief study of the thermodynamics of the C29/G41P scheme was undertaken. A typical tail gas stream to the CoMo reactor might have the composition shown in Table 1.

The exit gas composition listed is

Table 3

## Catalyst evaluation for COS hydrolysis

| **Test conditions:** | |
|---|---|
| Temperature, °F. | 300, 325, 365, 600 |
| Pressure, psig | 5 |
| Wet gas space velocity, V/V/hr | 2,000 |
| S/G Steam/gas | 0.40 |
| Feed gas, mole % | |
| CO | 0.450 |
| $CO_2$ | 7.68 |
| $H_2$ | 1-2.20 |
| $H_2O$ | 34.00 |
| $N_2$ | balance |

| | | Dry gas composition, ppm | | | |
|---|---|---|---|---|---|
| | | COS | $CS_2$ | $SO_2$ | $H_2S$ |
| 300° F. | | | | | |
| Inlet: | | 2,072 | 60 | 331 | 10,787 |
| Exit gas: | G41P | 243 | 35 | 2 | 10,650 |
| | C53-4 | 347 | 36 | Nil | 10,490 |
| 320° F. | | | | | |
| Inlet: | | 1,831 | 56 | 345 | 15,827 |
| Exit gas: | G41P | 250 | 9 | Nil | 13,334 |
| | C53-4 | 352 | 50 | 9 | 15,009 |
| 300° F. | | | | | |
| Inlet: | | 433 | 110 | — | 14,568 |
| Exit gas: | G41P | 4 | 28 | — | 14.778 |
| | C53-4 | 93 | 55 | — | 14,771 |
| 364° F. | | | | | |
| Inlet: | | 496 | 121 | — | 13,072 |
| Exit gas: | G41P | 3 | 2 | — | 14,727 |
| | C53-4 | 145 | 42 | — | 13,691 |

that expected (from calculations) when C29-2-03 is operated at 635° F. inlet (700° F. exit), 5 psig and a total wet gas space velocity of 1,000 v/v/hr.

The exit gas composition in Table 1 assumes complete conversion of $SO_2$, $CS_2$, and $S_n$, which has been seen to be the case in commercial operations as well as in the UCI laboratories.

As seen in Table 1, the equilibrium COS level exit the C29 reactor (at 700° F.) will be 12.6 ppm vol. However, if the gas is then cooled and passed over G41P at 350° F., the COS level should approach a level of 0.80 ppm vol, as the thermodynamics are much more favorable for COS hydrolysis at this lower temperature.

**Catalyst evaluation.** In order to determine the CoMo catalyst of choice for the hydrogenation step in this tail gas unit scheme, tests were conducted on United Catalyst Inc. (UCI) catalysts C25-2-02 and C29-2-03. The conditions used and results of these tests are summarized in Table 2. The results indicate that C29-2-03 is more effective here than C25-2-02. Later tests on C29-2-03 using a gas steam containing much higher $CO_2$, no COS, 6,800-14,250 ppm $SO_2$, and 17,000-22,050 ppm $H_2S$ again showed this catalyst to be very effective (>99%) for $SO_2$ hydrogenation.

The next phase of testing involved evaluating UCI catalysts G41P and C53-4 for the COS hydrolysis portion of this design. The results of these tests are shown in Table 3. Tests were conducted with and without $SO_2$ in the feed at the conditions listed below.

Results indicate that, at the conditions of these tests, G41P is the more effective of the two UCI catalysts for COS (and $CS_2$) hydrolysis. It is also seen that high levels of $SO_2$ can hinder COS hydrolysis. This is attributed to the fact that $SO_2$ can react with either COS or $CS_2$ to form $CO_2$ and elemental sulfur.

Table 4

## Deactivation test

| | | Dry gas exit | |
|---|---|---|---|
| | Dry gas inlet | Fresh C29-2-03 | Regen. C29-2-03 |
| COS, ppm | 347 | 40 | 145 |
| $CS_2$, ppm | 77 | ND | ND |
| $SO_2$, ppm | 2,374 | 6 | 133 |
| $H_2S$, ppm | 12,231 | 13,896 | 13,672 |
| $H_2$, % | 1.56 | ND | ND |
| CO, % | 1.15 | 0.05 | 0.05 |
| $CO_2$, % | 65.6 | 66.2 | 66.1 |

Table 5

## Split load test*

| | Dry gas inlet | Dry gas exit |
|---|---|---|
| COS, ppm | 382 | 36 |
| $CS_2$, ppm | 74 | ND |
| $SO_2$, ppm | 5,707 | 2 |
| $H_2S$, ppm | 12,598 | 13,468 |
| $H_2$, % | 2.56 | 1.05 |
| CO, % | 1.31 | 0.05 |
| $CO_2$, % | 65.9 | 66.5 |

*75/25 regenerated C29/G41P

In the early stages of the tests on G41P and C53-4, when $SO_2$ was included in the feedgas, elemental sulfur was found on the surface of the catalysts used in the test. This would be avoided if the $SO_2$ was converted to $H_2S$ in front on the COS hydrolysis bed, as it would be in the C29/G41P system.

**Split loading.** C29/G41P alignment described here is the more effective for TGCU applications. However, it has been recognized that in some instances it may be impractical to install a separate G41P vessel. With these instances in mind, one other possible alignment of C29-2-03 and and G41P was investigated for the hydrogenation/hydrolysis of the tail gas exiting a Claus unit.

In these tests, a 75/25 split loading of regenerated C29-2-03 (used in a commercial reactor prior to testing) and G41P was evaluated against a fresh loading of C29-2-03. CoMo catalysts normally experience a slight deactivation with time on stream in TGCU units.

We therefore felt that the addition of a layer of G41P in the bottom of the bed might allow operation of the CoMo reactor at acceptable COS levels for a longer period and thus prolong the life of the catalyst.

Regenerated C29-2-03 was used in the tests to approximate the level of deactivation that might be expected for this catalyst under normal operating conditions. The tests for this portion of the study were run at the following conditions:

| | |
|---|---|
| Pressure, psig | 5 |
| Temperature, °F. | 650 |
| Wet gas SV, v/v/hr | 2,000 |
| Steam/gas | 0.51 |

The first test was run to verify that the used C29-2-03 was partially deactivated. The results are shown in Table 4.

Once it was verified that the regenrated C29-2-03 was less active than fresh material, a 75/25 split loading of the used catalyst and G41P was tested at identical conditions with a similar feed gas (Table 5).

The results of this portion of the study indicate that the G41P catalyst for selective COS hydrolysis can be

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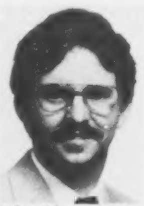
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used to return a reactor containing slightly deactivated CoMo catalyst to the level of performance achieved with fresh CoMo catalyst.

It was felt that if G41P is used with fresh C29-2-03 in this fashion, no immediate benefit of the COS hydrolysis catalyst would be seen because COS hydrolysis equilibrium is achieved with C29-2-03 alone at the higher temperatures used in the CoMo reactor.

However, test results indicate it should be possible to maintain acceptable COS emission levels longer if a layer of G41P is used in a 3/1 split loading with the C29-2-03 in the CoMo reactor. The effect of the G41P will be seen once the CoMo catalyst begins to deactivate, and the unit should give equilibrium COS levels (for the CoMo reactor temperature) longer than if C29-2-03 were used alone. It should be noted that G41P is not adversely affected by temperature in the 650-750° F. range.

The C29/G41P split-loading scheme is being used commercially in the Beavon reactor of a tail gas treating facility nominally rated to treat 30 MMscfd of gas from an offshore platform. The plant loaded 265 cu ft of C29-2-02 (same composition as C29-2-03, smaller particle size) on top of 90 cu ft of G41P.

In this instance, the volume of acid gas to the Claus/Beavon train is dependent upon the amount of sour gas recovered from an amine treating system. And because the $H_2S$ loading from the amine system has been light, the tail gas unit has been able to treat up to 60 MMscfd of offshore gas.

No conclusive data are available on the gas inlet and exit streams as yet, but reactor temperature profile data indicate that the catalyst loading is performing satisfactorily.

It should also be noted that, due to operating upsets, the inlet temperature reached 840° F. on one occasion and 900° F. on another. Despite this, the temperature profile indicates the C29 in the top of the bed is performing very well, because the bulk of the exotherm from hydrogenation reactions is still in the uppermost portion of the reactor, and the data that are available indicate that COS equilibrium is being achieved.

### Acknowledgments

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# Heat exchanger tube-bundle vibration is analyzed

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A short-cut method can be used to evaluate flow-induced vibrations. Preventing tube-bundle vibration is one of the major problems in the design of shell-and-tube heat exchangers.

Vibrations in the tube bundle are normally the result of fluid flow through the tube banks. They exist at almost every flow rate in which unbalanced forces are repeatedly applied to the tubes. The magnitude of these forces increases rapidly with increased fluid velocity.

But the unbalanced forces won't necessarily cause vibration unless a mechanical resonance leads to a large amplitude response. Vibration can also be caused by some interaction between the flow and the tube motion within the bundle, or at regions where flow enters or exits a nozzle.

Vibration can damage the tubes by a tube striking a baffle or by the tubes striking each other. Vibration can also cause fatigue cracking, generated by continuous stress on the tubes near a support such as the tube sheet.

Unfortunately, some of the thermal design techniques used today aggravate the vibration problem. For instance, the trend toward higher design flow velocities increases the susceptibility of the tubes to vibrate. Heat exchangers for high-density gases are designed for maximum velocity to achieve high heat transfer coefficients and to minimize fouling. Economical reasons, such as using fewer baffles and smaller-diameter tubes, also contribute to the vibration problem. When using the short-cut method detailed in this article to evaluate flow-induced vibrations, extra caution should be taken when there is a phase-change in the shell fluid, such as in condensers, where both inlet and outlet conditions must be computed and evaluated separately.

This method could be used for bare tubes or low-finned tubes. For finned tubes, root diameter and actual inside diameter are used for outside and inside diameter, respectively.

**Natural frequency.** Any tube can vibrate at different frequences. However, vibration is amplified at the

Table 1

## Strouhal numbers for common tube layouts

| Pitch to diameter ratio | Type of pitch: Triangular 60° | Rotated tri. 30° | Square 90° | Rotated sq. 45° |
|---|---|---|---|---|
| 1.25 | 0.79 | 0.18 | 0.42 | 0.60 |
| 1.33 | 0.75 | 0.22 | 0.36 | 0.60 |
| 1.40 | 0.70 | 0.25 | 0.32 | 0.60 |
| 1.50 | 0.62 | 0.29 | 0.30 | 0.57 |
| 1.67 | 0.47 | 0.33 | 0.28 | 0.51 |
| 1.75 | 0.41 | 0.34 | 0.27 | 0.47 |
| 2.0 | 0.28 | 0.35 | 0.26 | 0.28 |

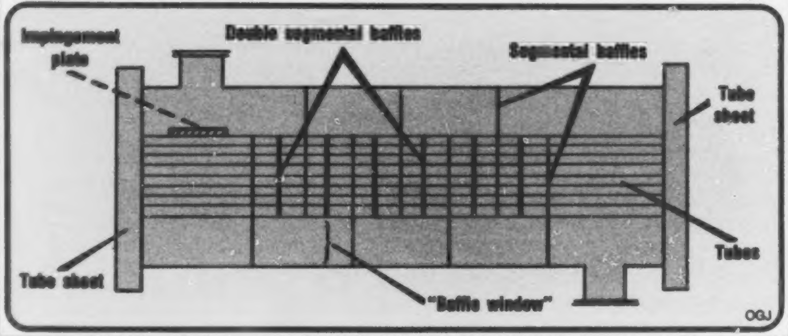
Table 2

## Values of the threshold constant, β, for typical tube layouts

| Pitch to diameter ratio | Type of pitch: Triangular 60° | Rotated tri. 30° | Square 90° | Rotated sq. 45° |
|---|---|---|---|---|
| 1.25 | 4.38 | 5.0 | 4.38 | 4.38 |
| 1.33 | 4.38 | 5.85 | 4.38 | 5.05 |
| 1.40 | 4.38 | 6.58 | 4.38 | 5.48 |
| 1.50 | 4.38 | 7.68 | 4.38 | 6.12 |
| 1.67 | 4.38 | 9.51 | 4.38 | 7.24 |
| 1.75 | 4.38 | 10.47 | 4.38 | 7.86 |
| 2.0 | 4.38 | 13.17 | 4.38 | 9.44 |

Fig. 1

## Vibration prevented by no-tubes-in-window design



tube's "natural frequency." If unbalanced forces are applied at driving frequencies that are at or near the tube natural frequency, resonance will occur, and the tube will experience high-amplitude vibration.

Straight-tube natural frequencies can be calculated by:

$$F_N = \frac{(3.36)(C1)}{(SP)^2} \times \sqrt{\frac{E \times I}{ME}} \quad (1)$$

where SP is span length. Other terms are defined in the nomenclature box. For a double span, use SP × 2.

The U-tube natural frequency is:

$$F_{NU} = \frac{(2.74)(CU)}{(RAD)^2} \times \sqrt{\frac{E \times I}{ME}} \quad (2)$$

Values for constants C1 and CU are given in TEMA[6] standards, 6th edition, pp. 224 and 228. RAD is the radius of U-bend. The effective mass per unit length of tube is:

$$ME = MT + MI + MO \quad (3)$$

where:

MT is the mass per unit length of tube:

$$MT = (OD)^2 - (ID)^2 \times 0.2226 \quad (4)$$

MI is the weight of fluid inside tube:

$$MI = \rho_t \frac{\pi \times ID}{4} \quad (5)$$

MO is the weight of fluid displaced by the tube:

$$MO = \rho_{SH} \frac{\pi \times OD}{4} \quad (6)$$

The second moment of area, I, is given by:

$$I = \frac{\pi}{64} [(OD)^4 - (ID)^4] \quad (7)$$

**Vortex shedding.** Tube vibration can be caused by vortex shedding. This type of vibration is the result of transverse periodic excitations caused by shell-side fluid flow across the bundle. Its magnitude is proportional to flow velocity. The frequency of this vibration is also called the "excitation frequency," and is believed to be independent of the Reynold's number within the range of 300 to 200,000.

The frequency can be expressed as:

$$F_{VS} = \frac{(S)(V)}{OD} \quad (8)$$

where S is Strouhal number, which is a function of tube geometry arrangements and variables such as the tube OD/pitch ratio. Its values are tabulated in Table 1.

Since shell-side flow mass is known from thermal design, cross-flow velocity between the tubes, V, can be computed by:

$$V = \frac{G_x}{\rho_{SH}} \quad (9)$$

**Critical velocity.** Fluid flow through a bundle causes an excitation in pressure fields above the tubes. At high

## Nomenclature

| | |
|---|---|
| A | Constant used in Equation 10 |
| AM | Min. cross-flow area of tube material at baffle, sq ft |
| BTH | Baffle thickness, ft |
| C | Velocity of sound, fps |
| CT | Min. clearance between adjacent tubes, ft |
| C1 | Mode constant used in Equation 1 |
| CU | Constant used in Equation 2 |
| D | Shell inside diameter, ft |
| E | Young's modulus of elasticity, lb/sq in. |
| $F_N$ | Tube natural frequency, hz |
| $F_{vs}$ | Vortex shedding frequency, hz |
| $F_{AC}$ | Acoustic resonance frequency, hz |
| FB | Factor used in Equations 12, 14 |
| $G_x$ | Shell cross-flow velocity, lb/sq ft-sec |
| G | Newton law constant = 32.174, $lb_m$-ft/$lb_f$-$sec^2$ |
| I | Second moment of area, $ft^4$ |
| ID | Tube inside diameter, ft |
| MT | Weight per unit length, lb/ft |
| MI | Weight of fluid inside tube, lb/ft |
| MO | Weight of fluid displaced by tube, lb/ft |
| ME | Effective mass per unit length of tube, lb/ft |
| MW | Molecular weight of gas |
| $N_D$ | Baffle damage number |
| $N_c$ | Collision damage number |
| OD | Tube outside diameter, ft |
| R | Gas constant = 1,545 lb/lb-mole-°R. |
| SM | Fatigue stress, lb/ft |
| SP | Baffle spacing, ft |
| T | Shell fluid temperature, °R. |
| V | Cross flow velocity between tubes, fps |
| $V_c$ | Connors critical velocity, fps |
| Z | Gas compressibility factor |
| $\beta$ | Threshold constant |
| $\gamma$ | Vapor specific heat ratio |
| $\rho_{SH}$ | Shell fluid density, lb/cu ft |
| $\rho_t$ | Tube fluid density, lb/cu ft |

fluid velocities and small tube spacing, the forces can be quite large, resulting in a velocity which depends upon fluid type, tube diameter, the natural frequency, damping, and mass ratio. This velocity known as the "Connors critical velocity" can be calculated by:

$$V_C = (\beta)(F_N)(OD)\sqrt{\frac{(0.03)(ME)}{(\rho_{SH})(OD)^2}} \quad (10)$$

Values of threshold constant, β, are shown in Table 2.

**Acoustical resonance.** There is always an acoustic wave frequency when gas or vapor is present in the shell-side fluid. An acoustic standing wave oscillates in the transverse direction (at right angles to the tubes). It is excited by cross flow over the tube bundle, should be compared against vortex shedding frequencies, and is given by:

$$F_{AC} = \frac{(A)(C)}{D} \quad (11)$$

where C is the velocity of sound:

$$C = \sqrt{\frac{(G)(\gamma)(R)(T)(Z)}{MW}} \quad (12)$$

The specific heat ratio of the gas, γ, is published in engineering handbooks, and the constant, A, is 0.50, 1.0, and 1.50 for the 1st, 2nd, and 3rd modes, respectively.

**Baffle damage.** Tube damage at the baffle is possible if shear stress caused by each span load exceeds the tube material fatigue stress. This damage can be expressed by the baffle damage number:

$$N_D = \frac{(OD)(\rho_{SH})(V)^2(SP)^2}{(FB)(SM)(G)(BTH)(AM)} \quad (13)$$

Values for the factor, FB, are 1.0 and 1.25 for tube to baffle hole clearance of 1/32 in. and 1/64 in., respectively.

Fatigue stress can be obtained from mechanical engineering hand books or estimated by: E/2400 for carbon steel and low alloy steel, and E/1000 for high alloy carbon steel and stainless steel (E is Young's modulus of elasticity).

The minimum cross flow area of the tube material, AM, at the baffle is:

$$AM = \frac{\pi}{4}\left[(OD)^2 - (ID)^2\right] \quad (14)$$

**Collision damage.** Collision damage may occur as a result of a large transverse deflection at the center of the span. In such cases, tubes can strike against adjacent tubes causing severe damage to each other.

The collision damage number is given as:

$$N_C = \frac{0.625(OD)(\rho_{SH})(V)^2(SP)^4}{(FB)^4(G)(AM)\left[(OD)^2 + (ID)^2\right]} \times CT \times E \quad (15)$$

where CT is the minimum clearance between adjacent tubes, i.e., CT = tube pitch − tube OD

The following procedure is recommended to check the possibility and severity of vibration:

Calculate the lowest tube natural frequency (at longest span), predominant Vortex shedding frequency, and

## Vibration analysis of typical heat exchanger

**Shell specifications**

Shell ID = 50 in.
No. of Baffles = 11 (No. of spans = 6)
Baffle spacing = 24 in.
Baffle thickness = 0.50 in.
Tube to Baffle hole clearance = 1/32 in.
Fluid density = 0.833 lb/cu ft
Cross flow velocity = 10.8 lb/sq ft-sec
Vapor molecular wt = 16.9
Specific heat ratio = 1.306
Compressibility factor = 1.0
Temperature = 20° F. = 480° R.

**Tube side specifications**

Tube OD = 0.625 in.
Tube ID = 0.505 in.
Tube pitch = 0.875 in.
Pitch type = Rotated sq
Fluid density = 4.206 lb/cu ft
Modulus of elasticity = 29 × $10^6$ lb/sq in.
Tube material = Carbon steel

**Analysis**

The mode constant is first obtained from TEMA, p. 224, for clamped-supported ends. At first mode, the constant, C1 = 32.37.

From Equation 9, V = 10.8/0.833 = 12.97 fps

**Natural frequency**

From Equation 7, I = 2.078 × $10^{-7}$ $ft^4$
From Equation 4, MT = 0.3622 lb/ft
From Equation 5, MI = .0059 lb/ft
From Equation 6, MO = 0.0018 lb/ft
From Equation 3, ME = 0.3622 + 0.0059 + 0.0018 = 0.3699 lb/ft

The natural frequency can be calculated from Equation 1 for double span tubes:

$$F_N = \frac{(3.36)(32.37)}{(2\times 2)^2}\left[\frac{(29\times 10^6)(2.078\times 10^{-7})}{0.3699}\right] = 27.403 \text{ hz}$$

**Vortex shedding frequency**

Pitch/diameter ratio = 0.875/0.625 = 1.4
From Table 1, for rotated square pitch, S = 0.60
From Equation 8:

$$F_{VS} = \frac{(0.60)(12.97)}{0.625/12} = 149.414 \text{ hz}$$

**Connors critical velocity**

From Table 2, = 5.48
From Equation 10;

$$V_C = (5.48)(27.403)(0.625/12)\sqrt{\frac{(0.3)(0.3699)}{(0.833)(0.625/12)^2}} = 17.332 \text{ hz}$$

Connors critical velocity. If the Vortex shedding frequency-to-natural-frequency ratio is greater than 5, or the cross flow velocity between tubes and Connors critical velocity ratio is greater than 0.69, vibration is probable.

When vapor is present in the shell, calculate the acoustical standing waves for different modes.

If the vortex shedding to acoustic frequency ratio is between 0.80 and 1.20, then tube vibration is likely to occur.

If the Thorngren baffle damage number or the collision damage number is greater than 1.0, then loud noise with possible tube damage is anticipated.

**Remedies.** There are some remedies:

- Use as many baffles as possible, to the maximum allowable shell pressure drop, to reduce the length of intermediate spans, which will increase the natural frequencies of the tubes.
- Design for "no tubes in baffle window" when an impingement plate is used (Fig. 1). Such design eliminates tubes from the top and bottom portion of the bundle, and no tubes will pass through the baffle cut. This method will also allow the use of double segmental baffles between the single segmental baffles, which provides more rigid support of the tubes.
- Minimize the shell-flow velocities and avoid excessive turbulence. This always tends to work against heat transfer and often requires major design modifications.
- Eliminate acoustical standing waves by reducing the shell diameter by using a longitudinal baffle to reduce the transverse width, and increase the resonant frequencies above the range of the Vortex shedding frequency. Also avoid rotated, square-pitch arrangements.
- Reduce the chance of vibration problems in U-tubes by providing extra support at the U-bend end of the bundle, and by lowering design velocity.

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- When an impingement plate is used, give additional support to tubes facing the incoming fluids at the edge of a baffle. Dummy tubes are often used in such circumstances to prevent tube damage.
- Avoid placing long spans at the inlet or exit sections of the tube bundle. If this cannot be prevented, provide extra support at the mid-point of the span for tubes passing through the baffle window.
- If thermally possible, design the shell for divided, cross, or split flow. This significantly reduces the possibilities of vibration.

In some cases, the source of vibration is not the heat exchanger itself, but is induced by mechanical resonance from plant equipment such as pumps.

This mechanical vibration is transmitted through the fluid. Engineers should check the complete plant layout for these types of equipment in order to avoid mechanical sources of vibration.

An example is shown in the box to demonstrate a vibration analysis of a typical shell-and-tube exchanger.

**Acoustical standing frequency:**

The velocity of sound from Equation 12:

$$C = \sqrt{\frac{(32.174)(1.306)(1545)(480)(1.0)}{16.9}} = 1357.89 \text{ fps}$$

From Equation 11:

$$\text{1st mode: } F_{AC} = \frac{(0.50)(1357.89)}{50/12} = 162.95 \text{ hz}$$

$$\text{2nd mode: } F_{AC} = \frac{(1.0)(1357.89)}{50/12} = 325.89 \text{ hz}$$

$$\text{3rd mode: } F_{AC} = \frac{(1.5)(1357.89)}{50/12} = 488.84 \text{ hz}$$

**Thorngren damage No.:**

For tube/baffle hole clearance of 1/32 in., $FB = 1.0$
Fatigue stress for carbon steel:
$= 29 \times 10^6/2400 = 12{,}083$ lb/sq in.
From Equation 14:
$AM = \pi/4\,[(0.625/12)^2 - (0.505/12)^2] = 0.00074$ sq ft

**Baffle damage No.:**

From Equation 13:

$$N_D = \frac{(0.625/12)(0.833)(12.97)^2(2 \times 2)^2}{(1.0)(12{,}083 \times 144)(32.174)(0.00074)(0.04166)}$$

$= 0.0677$ (double span)
$= 0.0169$ (single span)
$CT = 0.875 - 0.625 = 0.25$ in. $= 0.020833$ ft

**Collision damage No.:**

From Equation 15:

$$N_c = \frac{(0.625)(0.625/12)(0.833)(12.97)^2(2\times 2)^4}{(1.0)^4(32.174)(0.00074)[(0.625/12)^2+(0.505/12)^2](0.020833)(29\times 10^6)(144)}$$

$= 0.126$ (double span)
$= 0.0079$ (single span)
Vortex shedding/natural frequency = 149.414/27.403 = 5.45
Cross flow velocity/Connors velocity = 12.97/17.332 = 0.748
Vortex shedding/acoustical frequency: =
1st mode: = 149.414/162.95 = 0.9169
2nd mode = 149.414/325.89 = 0.4585
3rd mode = 149.414/488.84 = 0.3057

**Conclusions:**

Because the vortex shedding/natural frequency ratio is greater than 5, and the cross flow/Connors velocity ratio is greater than 0.69, vibration is highly probable in this heat exchanger design.

Acoustic resonance will certainly be excited in the 1st mode because the ratio 0.9169, falls between 0.80 and 1.20. But there is a low probability of tube damage because both baffle damage and collision damage numbers are less than one.

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# Advanced analyses improve delta coke prediction for resids

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Fluid catalytic cracking (FCC) of resid feedstocks requires a better prediction of delta coke—the difference between the coke deposited on the FCC catalyst and the coke remaining after catalyst regeneration.

Many people rely on feedstock Conradson carbon content alone to determine delta coke, but the relation between Conradson carbon and delta coke is not reliable for resid feeds (Fig. 1).

An advanced analysis of feedstock characteristics, coupled with a modified micro activity test (MAT), has been used to more accurately predict delta coke. A modified distillation procedure and a modified continuous pilot plant permit these advanced analyses. Results of the advanced analyses and procedures are expressed as the R2R index which correlates well with delta coke (Fig. 2).

**Delta coke relationships.** Delta coke is a major parameter in predicting FCCU operation on resid feeds. It determines primarily the temperature of the hot catalyst and whether the unit will be heat balanced.

Delta coke is affected by the catalyst, the feedstock, and the FCCU riser conditions.

There are three major reasons why delta coke prediction is important to the refiner:

1. The FCC feedstock gets a thermal shock when it is brought into contact with the hot catalyst. This thermal shock is very critical in processing resid-type feedstocks. The volatile part of the feed has to be evaporated quickly, while the asphaltenes have to shatter. The delta coke gives an indication of the thermal shock that can be applied to a given feed.

2. The FCC operation is preferably done without heat removal in order to minimize coke make and to maximize product yields. The delta coke gives an indication of the catalyst temperatures in the regenerator, affecting the activity of the catalyst.

3. The delta coke will indicate how well the unit is heat balanced.

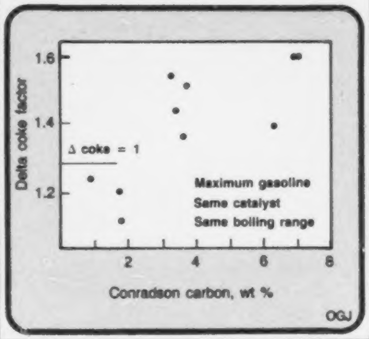
In our study on the influence of process parameters, a two-stage regenerator was used to provide the highest catalyst temperature without destroying the catalyst activity. No heat removal was applied (Fig. 3). The study was made to check the influence of the different parameters on the catalyst temperature in Regenerator 1 and in Regenerator 2.

The parameters used in the study are the delta coke, the coke quality (hydrogen and sulfur content), the amount of coke burned in the first regenerator, the $CO/CO_2$ ratios in the flue gas of the first regenerator, and the excess air in the second regenerator. Results of the study show (Table 1):

- Delta coke is the main parameter which determines the hot catalyst temperature. The other parameters have a second-order effect compared to the delta coke.
- The amount of coke burned in the first regenerator is a very effective parameter for con-

Fig. 1

## Delta coke predicted



trolling the first regenerator temperature to protect the catalyst, while achieving the most efficient thermal shock.

- The excess air in the second stage regenerator has limited influence on the hot catalyst temperature.

**Delta coke sources.** The catalyst, the feedstock properties, and the riser conditions all affect the formation of coke on the catalyst. Any attempt to predict the delta coke should take into consideration all of these parameters.

The tendency of the catalyst to coke, and its response to a change in the feedstock boiling range, must be known. In practice, there is a continuous search for low delta coke catalysts—low delta coke, but not at the expense of catalyst activity, conversion, and production quality.

The processing history (straight run, hydrotreated, thermally cracked), the boiling range, the Conradson carbon, the metals and alkalis, the nitrogen content, and the aromatic content of the feed all contribute to the tendency to make coke.

Table 1

## Influence of process parameters on regeneration

| Parameters | | Regenerator 1 | Regenerator 2 |
|---|---|---|---|
| Delta coke, wt % | base +0.5 | +60 | +100 |
| Coke burned in Regenerator 1, % | base + 20 | +45 | −13 |
| Excess air used in Regenerator 2, % | base + 20 | 0 | −8 |
| Effect of the coke hydrogen content, wt % | base −2 | −12 | −14 |
| Effect of CO/$CO_2$ ratio in Regenerator 1 | base +0.2 | −10 | −10 |
| Effect of sulfur in coke, wt % | base +2 | −2 | −2 |

Table 2

## Simulated distillation of feedstocks

| Feed 1 | | Feed 2 | | Feed 3 | |
|---|---|---|---|---|---|
| Temperature, °C. | wt % | Temperature, °C. | wt % | Temperature, °C. | wt % |
| 330 | — | 330 | — | 330 | — |
| 350 | 0.83 | 355 | 1.04 | 360 | 1.32 |
| 395 | 8.08 | 400 | 10.25 | 405 | 12.74 |
| 425 | 24.66 | 430 | 27.68 | 435 | 30.90 |
| 470 | 51.49 | 475 | 54.32 | 480 | 57.08 |
| 500 | 67.58 | 505 | 70.12 | 510 | 72.49 |
| 545 | 83.76 | 550 | 84.62 | 555 | 85.35 |
| 605 | 89.89 | 610 | 90.20 | 615 | 90.68 |
| 650 | 92.87 | 655 | 93.09 | 660 | 93.31 |
| 710 | 95.37 | 715 | 95.70 | 720 | 95.94 |

Nevertheless, such a feedstock characterization is an unsatisfactory predictor of coke formation because it does not differentiate between what we will call a "soft Conradson" and a "hard Conradson." In order to make a relevant delta coke prediction, it is necessary to go into more detailed feedstock analyses.

**Better analyses.** Distillation of the feed is necessary to check the cracking of the heavy ends, to develop correlations, to calculate the flash equilibrium of the feed at the riser inlet conditions, and to determine the portion that does not evaporate. The ASTM D1160 distillation is limited to about 565° C. which is too low a temperature when the processing of resid is contemplated.

At present, we use a simulated distillation technique developed by Total that allows temperatures up to 720° C. (1,328° F.) on a routine basis. We regard this temperature as a minimum in order to make a reasonable assessment of the distillation characteristics of a resid feedstock. Table 2 and Fig. 4 give examples of such distillations.

Our pilot tests indicate that typical parameters like aromatic carbon, Conradson carbon, nitrogen, contaminants, and boiling range do not prop-

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Based on a paper presented at the Ketjen Catalyst Symposium, Scheveningen, The Netherlands, May 26-28.

Fig. 2

## R2R improves delta coke prediction

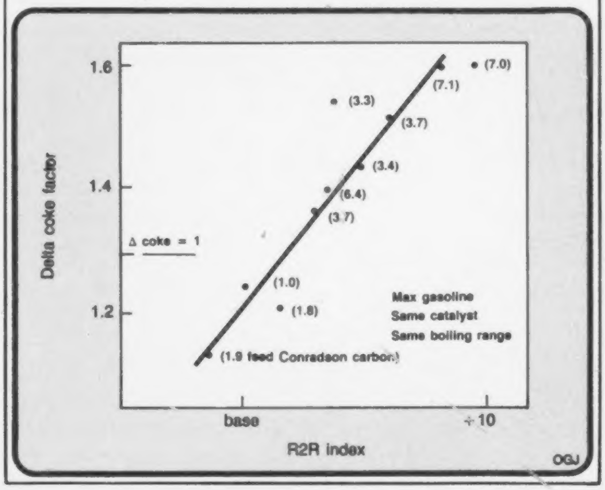


Fig. 3

## FCCU with two-stage catalyst regen

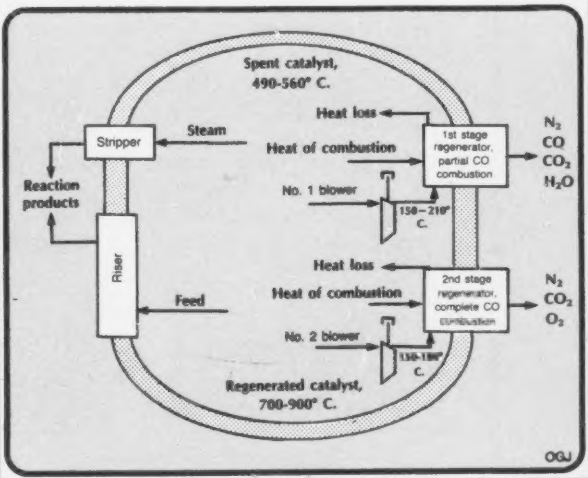
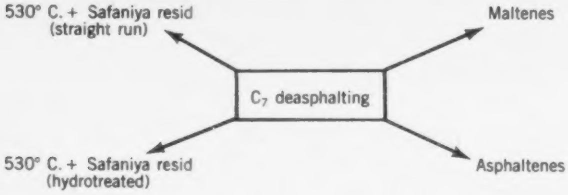


Table 3

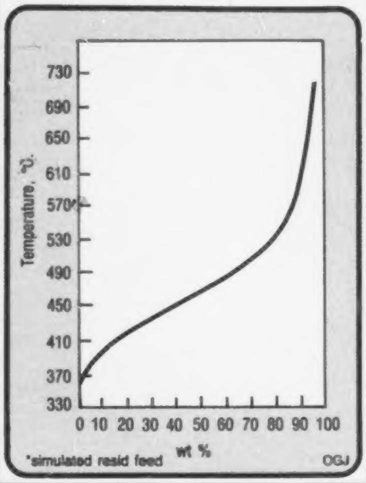
## Analysis of Safaniya resid



| | SR | HDT |
|---|---|---|
| Saturated | 28.1 | 26.4 |
| Mono and diaromatics | 9.0 | 8.7 |
| Other aromatics | 43.2 | 54.5 |
| Resins | 19.7 | 10.4 |
| | 100 | 100 |

Fig. 4

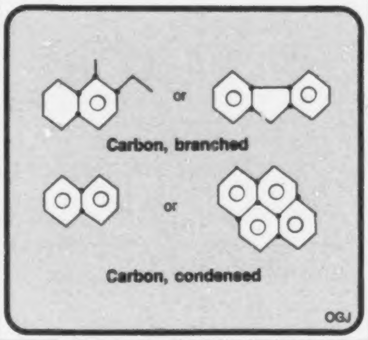
## Distillation curve



*simulated resid feed

Fig. 5

## Quaternary carbons



erly characterize resid feedstocks. The nuclear magnetic resonance technique (NMR) permits a more sophisticated characterization of a resid feedstock.

The aromatic carbons are split between quaternary carbons and protonated carbons. The quaternary carbons are further split between branched and condensed carbons (Fig. 5).

Tables 3 and 4 give an example. The same feed, first straight run then hydrotreated, has been analyzed through this technique. It should be noted in Table 3 that the technique is also applied for the C$_7$ asphaltenes.

This is a powerful tool to tackle the asphaltenes-cracking problem and to distinguish between hard and soft Conradson carbon. The aromatic fraction of hard Conradson carbon feedstocks tends to condense more and lead to higher delta coke than would be expected from the Conradson carbon value. Moreover, this sophisticated feedstock analysis enables us to develop what we call the R2R index which is quite effective to predict the delta coke and the coke make. This index is based on the NMR analysis of the aromatic fraction. It takes into account the degree of condensation, the type of aromaticity, and the hydrogen content.

**Riser reaction conditions.** The formation of coke on the catalyst is significantly affected by:

- The operating conditions (temperature and pressure)
- The riser hydrodynamics
- The feedstock evaporation, enhanced by the temperature of the hot catalyst and the size of the droplets issued from the injectors.

Fig. 6 illustrates the effect of the catalyst temperature on the speed of evaporation, and Fig. 7 shows the influence of 50 and 100 droplet size on the speed of evaporation. These data have been obtained from the continuous pilot plant.

- The thermal shock induced by the hot catalyst—This thermal shock is critical for the shattering of the asphaltenes present in the feed.

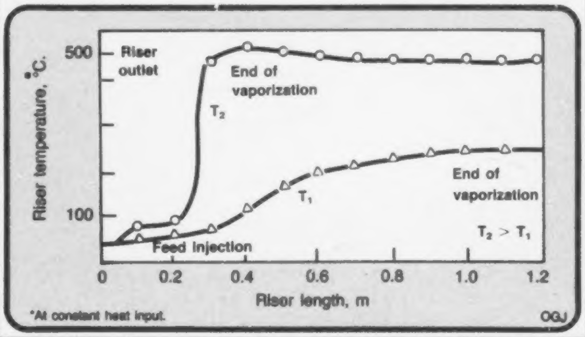
Fig. 8 illustrates the temperature profiles of the feed in an ASTM MAT and in the MAT with thermal shock. The coke and gasoline yields at the same conversion are given in Table 5 for both tests.

It has been found that coke yield is lower in the thermal shock MAT than in the ASTM MAT. Realizing the importance of a relevant coke/conversion relationship for delta coke prediction, thermal shock has been applied in our pilot plant facilities for developing the R2R process.

**Modified MAT.** When reviewing the parameters which affect the delta coke and the coke make, we have

Fig. 6

## Catalyst temp. vs. evaporation rate*



*At constant heat input.

Fig. 7

## Droplet size affects evaporation rate

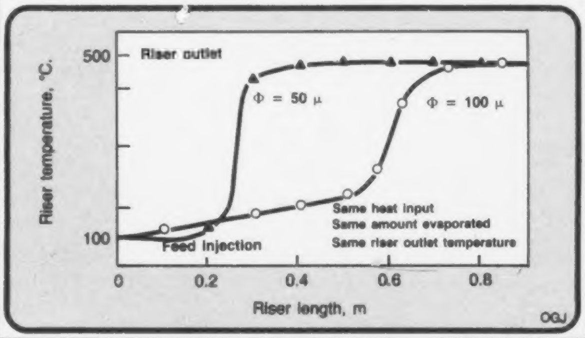
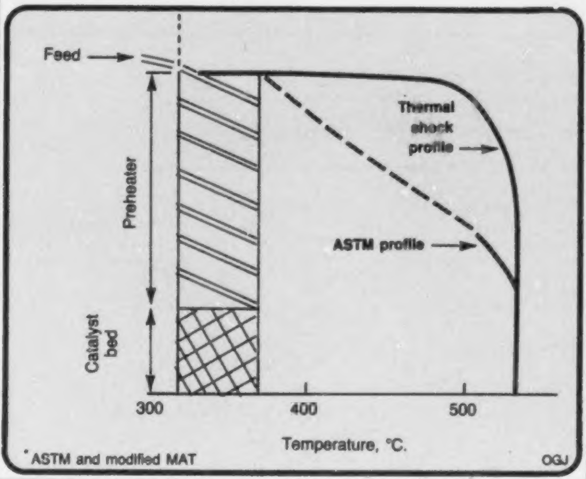


Fig. 8

## Temperature profiles*



*ASTM and modified MAT

Fig. 9

## Coke yield lower with modified MAT

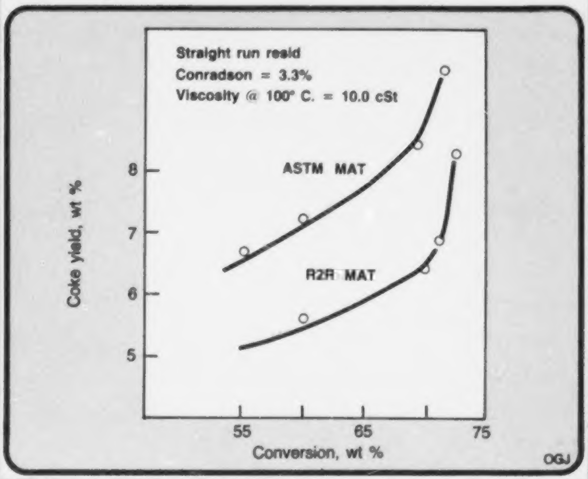


Fig. 10

## Low cat/oil ratios increase delta coke

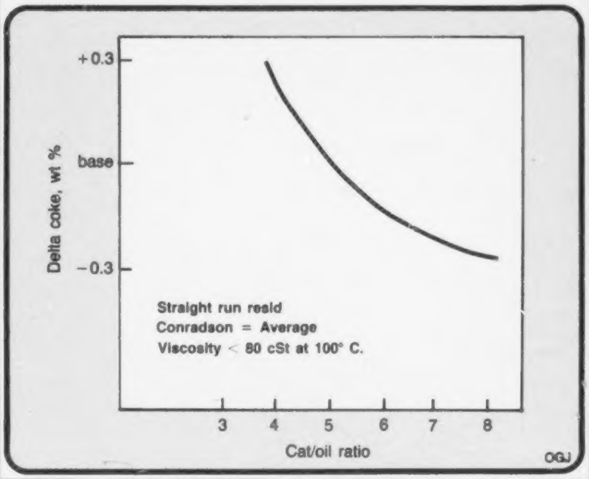
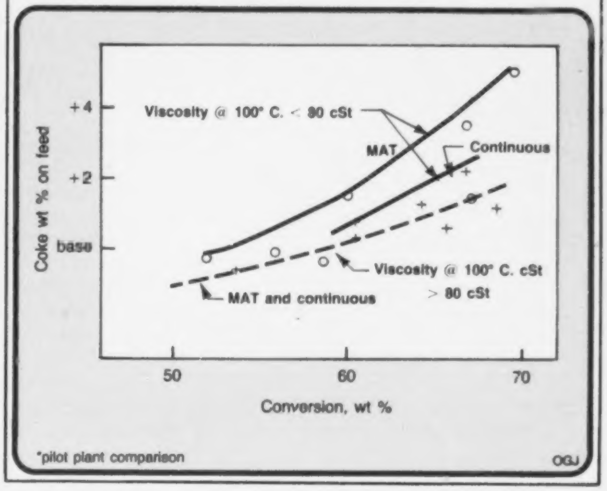


Fig. 11

## R2R MAT and R2R continuous*



*pilot plant comparison

Table 4

## NMR characterization of Safaniya resid*

| Aromatic carbon | Mono and diaromatics | | Other aromatics | | Resins | | Asphaltenes | |
|---|---|---|---|---|---|---|---|---|
| | SR | HDT | SR | HDT | SR | HDT | SR | HDT |
| Quaternary condensed | 6.1 | 3.9 | 12.9 | 9.8 | 10.4 | 13.9 | | |
| Quaternary branched | 15.6 | 11.0 | 17.6 | 17.8 | 15.4 | 16.4 | 42.7 | 49.6 |
| Protonated | 10.0 | 10.3 | 18.3 | 17.8 | 10.9 | 13.6 | 9.4 | 13.1 |
| Totals | 31.7 | 25.2 | 48.8 | 45.4 | 36.7 | 43.9 | 52.1 | 62.7 |
| Saturated carbon Quaternary | 3.0 | 2.6 | 3.3 | 3.7 | 3.1 | 6.1 | — | — |
| CH | 11.7 | 13.8 | 7.3 | 8.4 | 11.0 | 8.3 | — | — |
| $CH_2$ | 41.1 | 46.8 | 28.6 | 31.7 | 37.8 | 33.4 | — | — |
| $CH_3$ | 12.5 | 11.6 | 12.0 | 10.8 | 11.3 | 8.3 | — | — |
| Total | 68.3 | 74.8 | 51.2 | 54.6 | 63.3 | 56.1 | 47.9 | 37.3 |

*Straight run (SR) and hydrotreated (HDT) 530° C.+ resid.

Table 5

## Yield comparison of ASTM and modified MATs

| | ASTM profile | Thermal shock* |
|---|---|---|
| Conversion, wt % | 68 | 68 |
| Coke, wt % | base | −1.1 |
| Gasoline, wt % | base | +1.4 |

Feedstock: SR resid; $H_2$ = 12.7%, Ca = 16.3%
Catalyst: Ultrastable zeolite, Ni + V = 7,600 ppm
*Modified MAT

seen that the riser reaction conditions have a significant effect. The pilot plant must simulate these conditions in order to yield relevant information

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on resid feedstocks.

The standard ASTM MAT test cannot be used successfully with resid feedstock because there is no thermal shock, the atomization and the evaporation of the feed is poor, and the catalyst stripping unsatisfactory.

We have developed an advanced MAT pilot unit to simulate thermal shock conditions.

The feedstock atomization and evaporization is improved, and special care is taken for proper stripping of the catalyst. Fig. 9 compares the R2R advanced MAT test with the standard ASTM test.

The R2R approach works well with heavy feedstocks but is not fully satisfactory with very viscous feedstocks in the range of 80 cSt or more at 100° C. For these feeds, the thermal shock simulation and feedstock atomizing and evaporation still remain unsatisfactory.

We are still improving our MAT test since that test is fast and simple to carry out. Nevertheless, for very heavy and viscous feedstocks, a closer match of the operating conditions experienced in a full scale unit is necessary. The use of an advanced, continuous pilot plant facility is mandatory in order to develop relevant design data.

**R2R pilot plants.** One very important feature for the design of a continuous pilot plant is the simulation of the thermal shock along with very efficient feed atomizing. A second R2R continuous pilot unit has recently started up. It has improved thermal shock simulation and is highly flexible.

Fig. 10 illustrates the relationship between delta coke and C/O ratio when running our R2R continuous pilot plant facilities. Fig. 11 illustrates that for feedstocks having a viscosity up to 80 cSt at 100° C., the coke/conversion relationship is the same for the advanced MAT and the R2R continuous pilot unit.

For a viscosity higher than 80 cSt, it is obvious from the same figure that relevant coke yields are obtained only through the R2R continuous pilot unit.

### Acknowledgment

The authors thank M. Bourgogne, J.M. Colin, J.C. Courcelle of Total France, and A. Feugier and G. Martin of IFP for their contributions to this article.

# Two sampling techniques

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Two techniques are available to sample fluid catalytic cracking unit (FCCU) effluent vapors for unit performance evaluation. The reaction mix samples taken allow refiners to accurately check yields, product qualities, and operating conditions.

One sampling technique withdraws the vapor and separates the gas-liquid mixture at the unit. The other collects the sample in an aluminized polyester bag for separation and further analysis in the refinery laboratory.

**Two techniques.** In a reaction mix test, a sample of the total reactor effluent vapor is drawn before it enters the fractionator. The sample is taken at a slow rate over a period of time so that the short-term fluctuations in a commercial FCCU are smoothed out, and sufficient sample is obtained for further processing and analyses.

Flanders, et al., presented an "in situ" sample separation technique in which a sample-receiving train was attached to the operator end of a sample probe.[1] The hydrocarbon-vapor sample withdrawn from the FCCU is cooled, and the gas-liquid mixture is separated at the unit. Johnson and Fisher replaced the sample-receiving train with an aluminized polyester bag and reported that the new method was simpler and less time consuming.[2]

Chevron Research Co. and the former Gulf Research & Development Co. have made significant improvements in both techniques during the last few years. Several back-to-back comparisons of the two techniques have been made both in the laboratory and in refineries. With proper care, both techniques generate good results. These experiences have enabled Chevron Research to assess and further develop the advantages of each technique.

**Methods compared.** With in situ sample separation, representative samples are obtained by having a steady, well-controlled flow of hydrocarbon over a period of 30-40 min. This feature is especially important in refineries where operating conditions tend to have short-term fluctuations.

Because the light hydrocarbon gases are separated and vented immediately, large liquid samples can be obtained for product inspections. Also, because all of the sample handling is accomplished in situ, this technique requires no additional separation in the refinery laboratory.

In comparison, the bag technique requires less time, space, and equipment at the FCC sampling site. This makes it particularly well suited for units where harsh weather conditions exist, or where accessibility to the sampling area is limited.

Although large samples may be obtained with large or multiple bags, the bag technique is awkward for obtaining large samples for detailed product inspections. Also, because further sample handling is required, work space in the refinery laboratory is required. Back-to-back comparisons of the two techniques indicate that the total time required is about the same for both techniques. Consistency between the two techniques is about the same, as is the repeatability of both techniques. The standard deviation of the measured conversion is typically in the range of 1-1.5 liquid-vapor (LV) %.

**Sample probe.** A sample probe is required in both methods. Fig. 1 shows the probe assembly. This new design incorporates several features which previous probe designs do not have.[1] The body of the probe is made of ¼-in., Schedule 80, stainless steel pipe. The end of the probe (not shown) is sealed and perforated with small holes to prevent catalyst from plugging the probe.

A gate valve (No. 1, Fig. 1) has replaced the previous globe valve to minimize plugging. As a safety measure, a ball valve (No. 3) with a quick shut-off handle is placed in series with the gate valve. Both valves have been rated for high temperature and pressure applications. The valves are welded to the probe (No. 17) to avoid removal or accidental break-off.

A safety chain (No. 7) is permanently welded to the flat bar (No. 5) and packing gland flange (No. 8) to pre-

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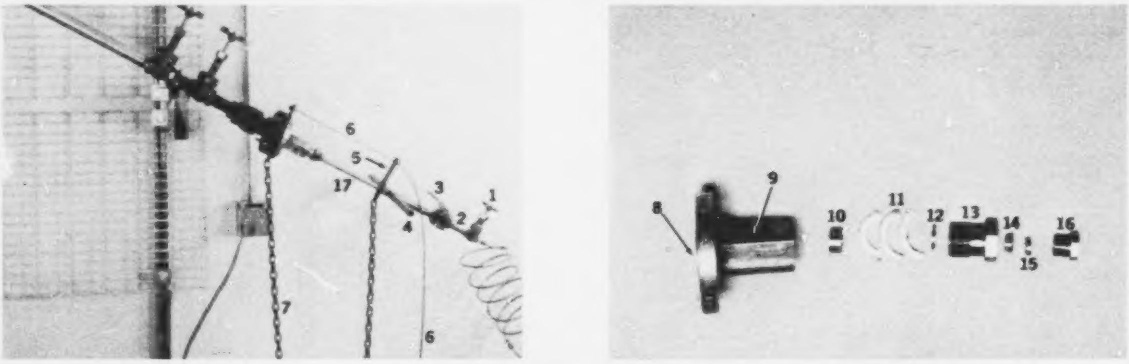
Based on a paper presented at the American Petroleum Institute 51st Midyear Refining Meeting, San Diego, May 12-15.

# accurately evaluate fluid-cat-cracking products

Fig. 1

Sample probe



1. ¼ in. SS gate valve
2. ¼ in., Sch. 80 × 3 in. nipple
3. ¼ in. SS Highper Mizer ball valve
4. ½ in., Sch. 80 SS pipe
5. ¼ in. × 1-in. wide SS flat bar
6. ¼-in. OD SS cable indicator
7. SS safety chain
8. 1 in., Class 300 packing gland flange, SS
9. Body packing gland
10. Front spacer washer
11. Packing material
12. Rear spacer washer
13. Packing gland nut
14. Front brass ferrule
15. Rear brass ferrule
16. Lock nut
17. Probe, ¼ in., Sch. 80 SS pipe
18. 1 in. R.F. gasket

OGJ

vent removal of the probe from the packing gland (No. 9). As an additional precaution, a cable indicator (No. 6) attached to the probe serves as a positive indicator of the position of the probe in the reactor effluent vapor line. The new design for the packing gland features two control nuts which provide both a tight seal and easy removal of the probe. The packing gland nut (No. 13) controls the packing tightness, while tightening the locknut (No. 16) prevents probe movement.

**Port preparation.** If a sample port has not been used for a few days, it is probably blocked by coked catalyst and must be drilled out. This is accomplished by using a 9/16-in. masonry bit welded to a ½-in. shaft which is long enough to go through the packing gland and into the reactor-effluent vapor line.

Because the vapor line is usually under a pressure of 10-20 psig, and a temperature of up to 1,000° F., extreme care must be taken when drilling out the port.

The drill bit is slightly larger than the opening in the packing gland to prevent accidental removal. Thus, prior to drilling, the drill shaft is inserted through the drill assembly packing gland from the vapor-line side of the packing gland.

The sample port in the refinery is usually equipped with two block valves upstream of the sample port flange. Prior to drilling, the operator must make sure that both block valves are closed. The blind flange is then removed from the sample port.

The packing gland is installed on the sample port flange and tightened. The operator then slowly opens the block valves and watches carefully for any hydrocarbon leaks. Any leaks can usually be stopped by tightening the packing gland nuts.

Coke deposited in the sample port is slowly drilled out with an air-operated drill motor equipped with a ½-in. chuck. Again, any hydrocarbon leaks must be stopped immediately.

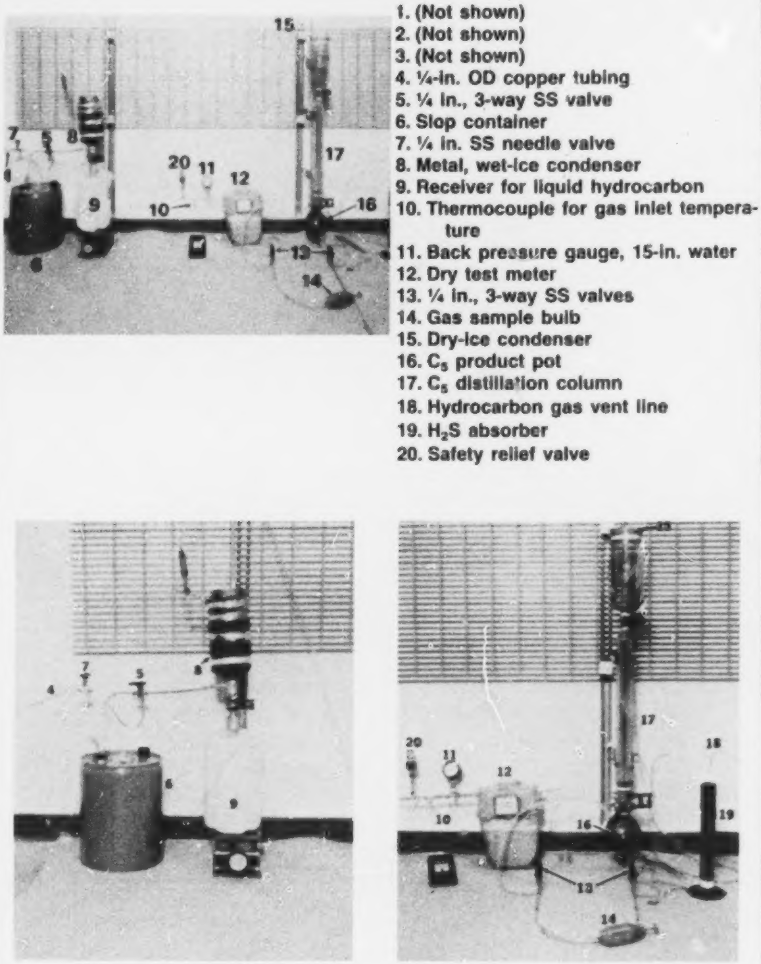
**Installation and removal.** A representative sample of the hydrocarbon vapor is obtained by using a small pipe for the probe, positioning the end of the probe in the center of the reactor effluent vapor line, and sloping the probe downward from the vapor line. Improper installation is often the cause of inconsistent and poor results.

Prior to installation, the probe is cleaned and the packing gland inspected in the laboratory. The safety chain must be short enough so that the tip of the probe cannot pass the packing gland when the probe is pulled away from the sample port. The sample port block valves and the valves on the probe must be closed before removing either the blind flange or the drill assembly packing gland from the sample port, and before installing the probe packing gland on the sample port flange. After inserting the probe as far as the outside block valve, the operator tightens the packing gland and adjusts the cable indicator so that it is straight between the holding plates. The movable clamp on the cable indicator is then installed so that it rests against the operator side of the flat bar.

After checking that the gate and ball valves on the probe are closed, the block valves for the sample port are opened, and the probe is pushed into

Fig. 2

## In situ sample separation train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1. (Not shown)
2. (Not shown)
3. (Not shown)
4. ¼-in. OD copper tubing
5. ¼ in., 3-way SS valve
6. Slop container
7. ¼ in. SS needle valve
8. Metal, wet-ice condenser
9. Receiver for liquid hydrocarbon
10. Thermocouple for gas inlet temperature
11. Back pressure gauge, 15-in. water
12. Dry test meter
13. ¼ in., 3-way SS valves
14. Gas sample bulb
15. Dry-ice condenser
16. $C_5$ product pot
17. $C_5$ distillation column
18. Hydrocarbon gas vent line
19. $H_2S$ absorber
20. Safety relief valve

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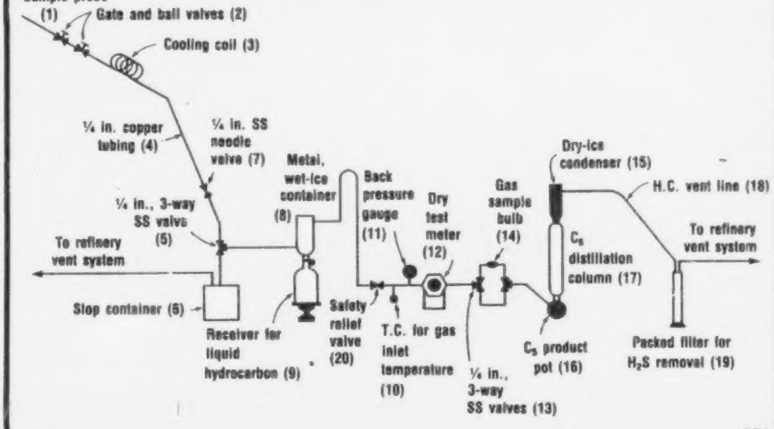
Fig. 3

## Flow diagram of in situ separation train


Sample probe (1)
Gate and ball valves (2)
Cooling coil (3)
¼ in. copper tubing (4)
¼ in. SS needle valve (7)
Metal, wet-ice container (8)
¼ in., 3-way SS valve (5)
To refinery vent system
Slop container (6)
Receiver for liquid hydrocarbon (9)
Back pressure gauge (11)
Safety relief valve (20)
Dry test meter (12)
T.C. for gas inlet temperature (10)
Gas sample bulb (14)
¼ in., 3-way SS valves (13)
Dry-ice condenser (15)
C₅ distillation column (17)
C₅ product pot (16)
H.C. vent line (18)
To refinery vent system
Packed filter for H₂S removal (19)

OGJ

the reactor-effluent vapor line. As the probe is further inserted into the sample port, the distance between the two holding plates is shortened. The resulting excess length of cable is the same as the distance that the probe has traveled and, therefore, serves as an indicator for the position of the probe. After finishing all of the reaction mix tests, the operator closes the gate and the ball valves on the sample probe and withdraws the probe to clear both sample port block valves using the cable indicator as a guide. The safety chain prevents the probe from being accidentally pulled out of the packing gland.

The operator then closes the block valves, removes the packing gland with the probe, and reinstalls the blind flange on the sample port.

**Sample separation train.** Fig. 2 shows the in situ sample separation train. Fig. 3 is a schematic of the arrangement. This arrangement is significantly different from what has been previously reported.[1] A stainless- steel cooling coil (No. 3, Fig. 3) is installed immediately after the probe (No. 1) so the copper tubing (No. 4) connecting the coil to the main part of the receiving train receives cool effluent. The copper tubing is positioned downward from the probe to the condenser (No. 8) to ensure that all condensate is collected.

A needle valve (No. 7) controls the flow rate of the hydrocarbon sample. A three-way valve (No. 5) diverts the flow to either a slop container (No. 6) or a wet-ice condenser (No. 8) which separates the hydrocarbon flow into a liquid and a vapor. The glass liquid receiver (No. 9) is externally coated with a thin film of Teflon and protected with a Nalgene acid carrier. Use of glassware is minimized. The rest of the glassware is protected with Polynet plastic wrappers.

The vapor coming out of the wet-ice condenser flows upward to minimize the entrainment of liquid condensate. It then flows through a safety relief valve (No. 20), a backpressure gauge (No. 11), a thermocouple (No. 10), and a dry test meter (No. 12). The safety relief valve (No. 20) should be preset at 1 psig in the laboratory.

Controlled by two 3-way valves (No. 13), the vapor flows through either a bypass line or a gas-sample bulb (No. 14) before it goes into a $C_5$ product pot (No. 16). The vapor flows up the $C_5$ distillation column (No. 17) and is cooled with a dry-ice condenser (No. 15). Acetone is used in the dry-ice condenser to make sure that all the $C_5$s are condensed in the liquid sample. Because acetone may cause eye and skin irritation, and is extremely flammable, it must be handled with extreme care.

Chevron Research recommends that not more than 1 gal of acetone be present in the reaction mix test area. Acetone must be stored in a metal safety can designed for fire-protective storage of flammables. An example is a Justrite metal can equipped with double-wire mesh flame arrestors for fast pour-through and a leak-tight, self-closing spout for automatic pressure relief. Care must be taken not to spill any acetone during pouring.

The condensed liquid is collected in the $C_5$ product pot. The uncondensed vapor flows through a hydrogen sulfide absorber (No. 19) before it is vented. A special chemically coated charcoal (Ventsorb IVP), contained in a sealed plastic pail, is used to absorb $H_2S$.

The hydrocarbon gas is typically vented at a rate of 0.1 scfm. If possible, the vent lines should be connected to an existing refinery vent system at atmospheric pressure. If this is not feasible, the hydrocarbon gas must be carefully vented downwind from the sampling site, and away from any potential ignition source.

**Bag-collection train.** Fig. 4 shows a diagram of the bag used. Although many types of bags are available, Chevron Research chooses to use a bag made from a five-layer bonded material which has excellent product-retention qualities, especially for hydrogen. The five layers consist of polyethylene, polyamide, aluminum foil, polyvinyl dichloride, and polyester. Several standard sizes of bags are available from the vendor.[3] The 44-l. and the 70-l. sizes are found to be most convenient for reaction mix sampling. Because of some difficulties experienced with the valves, bags with straight-through connections are preferred.

Fig. 4

Sample bag diagram

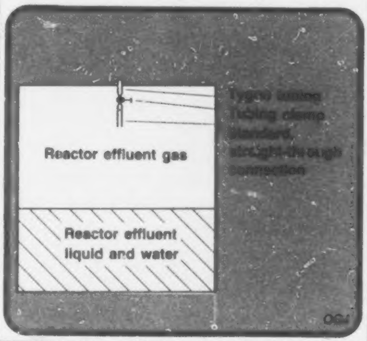

Tygon tubing
Tubing clamp
Standard, straight-through connection
Reactor effluent gas
Reactor effluent liquid and water
OGJ

Fig. 5 shows the arrangement of a bag collection train. A three-way valve (No. 6, Fig. 5) is connected to the stainless steel coil (No. 3) to divert hydrocarbon vapor flow to either the sample bag (No. 9) or the slop container (No. 7). A 10-in. Hg manometer (No. 5) is used to ensure that the bag is not overpressurized. Sampling rate is set with a needle valve (No. 4).

**In situ separation.** Prior to taking samples, the operator weighs all the liquid receivers and fills the ice condenser (No. 8, Figs. 2 and 3) with ice and water, and the dry-ice condenser (No. 15) with dry ice and acetone. For each reaction mix test, four sets of yield period samples are taken, the first of which is simply to wet the condenser. The products are thrown away. For each yield period sample, the hydrocarbon flow is regulated with the needle valve (No. 7) to about 0.1 scfm. At this rate, a yield period typically lasts 30-40 min in order to collect at least 800 g of liquid product. This quantity is sufficient for gasoline octane determinations and other product inspections. Water, ice, dry ice, and acetone are added to the condensers as needed during the course of the test. The temperature of the dry-ice condenser (No. 15) is carefully monitored so that the temperature remains below −30° F., as indicated by the condenser thermocouple.

For each yield period, two hydrocarbon gas samples are taken—one about 10 min after starting a yield period, and the other about 20 min after starting a yield period. This is accomplished by switching the hydrocarbon gas flow through a gas bulb with the three-way valves (No. 13).

Both the rate and the total flow of the gas are recorded. At the end of a yield period, the total liquid weight is recorded and a vial of liquid taken for gas chromatograph (GC) analysis.

After finishing a yield period, the hydrocarbon vapor is diverted to the slop container (No. 6) with the three-way valve (No. 5). The operator then partially debutanizes the liquid in the $C_5$ receiver (No. 16) with warm water and adds the remaining oil to the products in the liquid receiver (No. 9).

Including all of the $C_5+$ components in the liquid is important to properly determine light gasoline octanes. Partially debutanizing the $C_5$ receiver liquid reduces the vapor pressure of the total liquid, which, along with other samples, is usually shipped back to Chevron Research for further processing.

**Bag procedure.** The bag technique requires less equipment and sample workup in the vicinity of the sample probe. Care must be taken not to tear or puncture the bags.

After proper setup, the sample port block valves are opened and the sam-

Fig. 5

Bag collection train

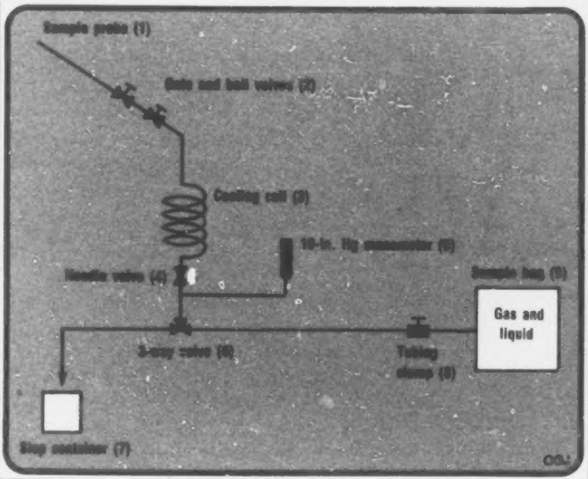

Sample probe (1)
Gate and ball valves (2)
Cooling coil (3)
10-in. Hg manometer (5)
Needle valve (4)
Sample bag (9)
Gas and liquid
3-way valve (6)
Tubing clamp (8)
Slop container (7)
OGJ

Fig. 6

Bag procedure vapor-liquid separation

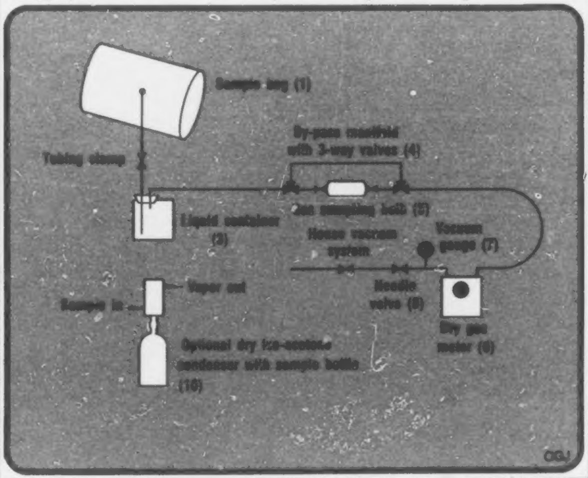
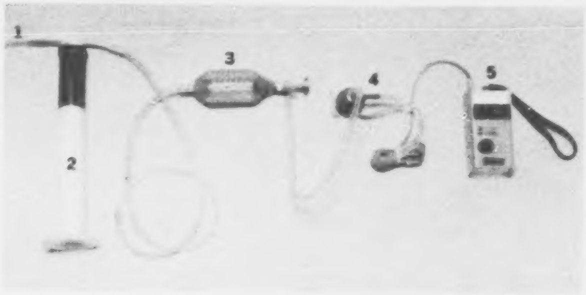

Sample bag (1)
By-pass manifold with 3-way valves (4)
Tubing clamp
Gas sampling bulb (5)
Liquid container (3)
House vacuum system
Vacuum gauge (7)
Needle valve (8)
Vapor out
Sample in
Dry gas meter (6)
Optional dry ice-acetone condenser with sample bottle (10)
OGJ

Fig. 7

## Flue gas sampling system

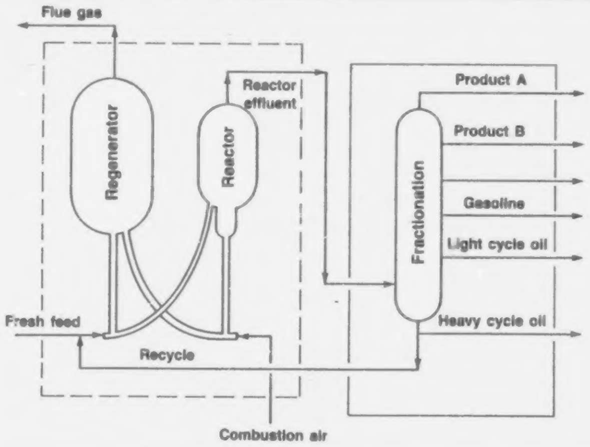


1. Flue gas line 2. Moisture absorber 3. Gas sample bulb
4. Oxygen sensor 5. Portable $O_2$ analyzer

OGJ

Fig. 8

## FCCU mass balance envelopes



OGJ

ple flow adjusted with the needle valve (No. 4, Fig. 5) to collect 30-50 ml of liquid/min, measured by replacing the slop container (No. 7) with a graduated cylinder. The operator allows about 5 min to purge the sample system before switching the three-way valve (No. 6) to direct sample flow to the bag (No. 9).

The bag is filled to no more than 80% capacity to prevent pressure buildup as a result of possible temperature change. When the bag is nearly full, the operator turns the three-way valve (No. 6) to direct flow back to the slop container before clamping the Tygon tubing (No. 8) and removing the bag. Three or four bags are typically taken for each test.

After the tests, the bag samples are placed in the refinery laboratory for approximately 3-4 hr so that vapor-liquid equilibrium is achieved. If the outdoor temperature is significantly below the laboratory temperature, the equilibration is accomplished in a sheltered outdoor location so that the bag is not overpressurized due to vapor expansion. Fig. 6 is a schematic diagram of the laboratory setup for separating and preparing the vapor and liquid portions of the reaction mix samples for shipment. The bag (No. 1, Fig. 6) is connected to a standard liquid container (No. 3) with a tube and rubber stopper.

A second tube connects the container to a vapor-sampling manifold (No. 4) and a dry test meter (No. 6). The meter outlet is connected to the laboratory's explosion-proof vacuum system (No. 9). Prior to connecting the gas meter to the manifold, the needle valve (No. 8) is set to allow vapor flow at a rate for which the meter has been calibrated; usually in the range of 0.1-0.5 scfm.

The sample manifold is set to direct flow through the gas-sampling bulb (No. 5), with the three-way valves and the sample bulb valves open. The bulbs are not evacuated prior to use because this would alter the volume of the gas metered.

The tubing clamp on the bag (No. 2) and the valve to the house vacuum system (No. 9) are opened simultaneously. The bag is positioned with the tube connection on the bottom to facilitate liquid flow.

When the bag is about one-third empty, the manifold (No. 4) is switched to bypass, bulb valves closed, and the sampling bulb removed. A second gas sample is taken when the bag is about two-thirds empty. This assures complete purging of all air from the sampling bulbs.

The bag is empty when a slow increase of volume is noted on the gauge. The empty bag is weighed, flushed with solvent, and reweighed to account for liquid holdup. Excellent flushing results are obtained by vacuuming out the flush liquid, inflating the bag with air, and revacuuming. Naphtha, hexane, and acetone have been successfully used for flushing. Acetone, however, dissolves the bag's rubber gaskets and prevents it from being reused.

Alternatively, if large or multiple bags are used to obtain a sample sufficient for product inspections, a dry ice and acetone condenser (No. 10) may be substituted for the liquid container (No. 3). This ensures that all $C_5$s are captured for accurate light gasoline octane determination.

**Flue gas sampling.** In addition to hydrocarbon samples, flue gas samples are required during a reaction mix test in order to calculate the coke yield and the heat balance of the FCCU. Because of the fluctuations in flue gas composition, the best results are obtained by taking a small stream of flue gas with a sample bag over a period of 5-10 minutes. After the test, the bag is taken into a refinery laboratory and emptied by connecting it to a vacuum line. Two samples are taken for GC analyses when the bag is about one-third and two-thirds empty, respectively. Alternatively, bulb samples can be taken directly from the flue gas sampling line. Fig. 7 shows the arrangement for on-line sampling.

It is important that the operator monitors the reading on the portable oxygen analyzer (No. 5, Fig. 7) and waits for a relatively stable period before taking a sample. The high and low readings should be within about 0.5 vol %. Two samples are taken for each yield period at about 10 and 20 min after the yield period starts.

## The authors. . .

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**English**

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**Analytical.** At Chevron Research, the reaction mix gas and the flue-gas samples are analyzed with a GC for components up to $C_6$. The light ends content of the liquid sample is also determined with a GC.

If product inspections are required, the liquid sample is distilled to generate debutanized light gasoline, heavy gasoline, light cycle oil, medium cycle oil, and heavy cycle oil. On the other hand, if only yield data are required, a GC-simulated distillation provides a lower cost and faster alternative to batch distillation.

In cases where the FCCU does not have a recycle stream, a complete yield structure can be calculated by combining the liquid distillation and the GC results.

On the other hand, if a recycle stream is present, its contribution to the product samples must be properly accounted for. Fig. 8 shows the flow pattern of a typical FCCU. If an envelope is drawn around the reactor-regenerator (dashed line in Fig. 8), the mass balance equation is:

$$\text{FF} + \text{R} = (\text{FG} - \text{Air}) + \text{RE} \qquad (1)$$

or

$$\text{RE} = \text{FF} + \text{R} - \text{Coke} \qquad (2)$$

where:

RE = Mass flow rate of reactor effluent, lb/hr
FF = Fresh feed rate, lb/hr
R = Recycle rate, lb/hr
Coke = Coke burned, lb/hr
FG = Flue gas rate, lb/hr
Air = Combustion air rate, lb/hr

The rate of any specific product component (molecular species or liquid boiling range) is obtained by a balance around the product-recovery system shown as a solid line envelope in Fig. 8.

$$\text{A} = (\text{CA re})(\text{RE}) - (\text{CA r})(\text{R}) \qquad (3)$$

where:

A = Mass flow rate of any prouct component (either individual molecular species or TBP boiling range), lb/hr
CA re = Fraction of Component A in the reactor effluent,
CA r = Fraction of A in the recycle

Combining Equations 2 and 3 gives:

$$\text{A} = (\text{CA re})\,(\text{FF} + \text{R} - \text{Coke}) - (\text{CA r})(\text{R}) \qquad (4)$$

$$\text{A, wt \% FF} = [(\text{CA re})\,(\text{FF} + \text{R} - \text{Coke}) - (\text{Ca r})\,(\text{R})]*100/\text{FF} \qquad (5)$$

This equation requires only three flow rates (fresh feed, recycle, and combustion air) and a few inspections (fresh feed gravity, recycle gravity and distillation, effluent analysis, and flue gas analysis). However, it requires accurate measurement of the recycle rate. An alternative method avoids the need to measure the recycle rate. Equation 4 can be rearranged to be explicit for the recycle rate:

$$\text{R} = [(\text{CA re})\,(\text{FF} - \text{Coke}) - \text{A}]/(\text{CA r} - \text{CA re}) \qquad (6)$$

We may define A as the material that is heavier than a certain TBP boiling cut point (e.g., 430° F. as measured by fractionator product flow meters and corrected for boiling range overlaps. (CA r = 1 and A = 430+) where 430+ is the liquid product boiling above 430° F. as measured by fractionator product flow meters and corrected for boiling range overlaps.

Equation 6 becomes:

$$\text{R} = [(\text{CA re})\,(\text{FF} - \text{Coke}) - 430+]/(1 - \text{CA re}) \qquad (7)$$

Equation 7 provides the basis for the second calculation method. This method relies on the meter reading for heavy cycle oil. This is usually more accurate than the recycle rate which is difficult to measure because of catalyst fines in the stream. Once the recycle rate is calculated using Equation 7, product yields can be calculated using Equation 5.

In the explanation above, it was convenient to define "A" as a liquid boiling range which included all the recycled material. This made CA r = 1 and eliminated the need for analyzing the recycle stream. On the other hand, if reliable recycle composition data are available, "A" may be defined as a narrow boiling range which is found in only one product stream. In this case, only the flow rate of this particular product stream is required.

Because of the variety of FCC units within Chevron and the diversity of their locations, the operating strategies and product objectives differ from refinery to refinery. As a result, the requirements for reaction mix test vary. The flexibility of using both in-situ and bag-sampling techniques lets Chevron Research support the ever-changing needs of its refineries.

**References**

1. Flanders, R.L., Annesser, F.J., and Saville, D.A., "Cat cracker analysis simplified," OGJ, Jan. 9, 1961, p. 84.
2. Johnson, A., and Fisher, I.P., "Bag sampling aids FCCU studies," OGJ, Feb. 11, 1985, p. 98.
3. Calibrated Instruments Inc., 731 Saw Mill River Road, Halsley, New York 10502.

# Droplet settling theory key to

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Droplet settling theory can be used to understand many of the empirical correlations in use today for sizing gas/liquid separators and trayed columns.

It is possible to predict design liquid droplet diameters, which explain those correlations. Once the design droplet is determined, the results can then be extrapolated to other fluid properties or can be used as a scaling factor for field or bench tests.

This relationship will then be applied to some well known correlations in use in industry today for sizing gas-liquid separators. This will be done to show that the correlations are better understood in terms of droplet settling than in terms of some mysteriously derived "K" factor or capacity given by a vendor.

Once the correlation is stated in terms of droplet settling, including all pertinent fluid properties, one then becomes more secure in extrapolating the data to situations involving much different flowrates and fluid properties.

**Theory.** The gas/liquid separation problem in a vertical vessel can be modeled as shown in Fig. 1. As the gas moves vertically upward in the vessel, droplets of the liquid entrained within the gas tend to fall vertically downward relative to the gas due to gravity.

Each droplet accelerates due to this negative buoyant force until the drag force on the droplet equals the buoyant force.

At this point, acceleration goes to zero and the droplet reaches its terminal velocity ($V_t$). If the terminal velocity slightly exceeds the upward flowing velocity of the gas ($V_g$), then the droplet will settle relative to the gas phase and the droplet will separate from the gas.

If $V_t$ is slightly less than $V_g$, the droplet will be carried upward by the gas phase and not be separated.

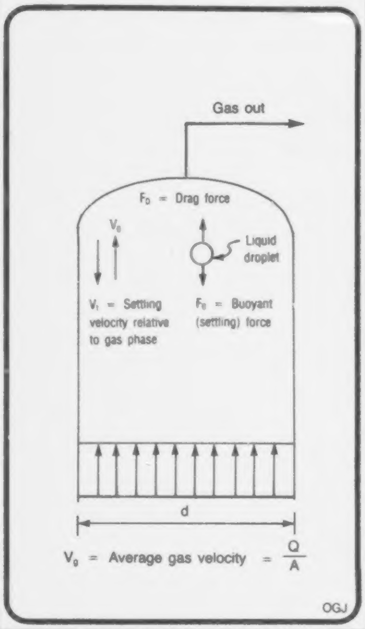
The nomenclature used in the relationships presented in this article appears in the accompanying box.

The buoyant force depends on droplet volume and the difference between droplet density and the density of the surrounding gas:

$$F_B = (\rho_l - \rho_g)\ (\text{droplet volume}) \quad (1)$$

Fig. 1

Vertical separator


Gas out
F_D = Drag force
V_g
Liquid droplet
V_t = Settling velocity relative to gas phase
F_B = Buoyant (settling) force
d
V_g = Average gas velocity = Q/A
OGJ

## Nomenclature

$A$ = Vessel cross-sectional area, sq ft
$A_d$ = Droplet cross-sectional area, sq ft
$D$ = Droplet diameter, ft
$d$ = Required vessel internal diameter, in.
$d_m$ = Droplet diameter, microns
$C$ = Drag coefficient from API 521
$C_D$ = Drag coefficient from Equation 4
$F_B$ = Buoyant force, lb
$F_D$ = Drag force, lb
$g$ = Gravitational acceleraton, fps$^2$
$K$ = Empirical factor
$MW$ = Gas molecular weight
$P$ = Operating pressure, psia
$Q$ = Gas flow rate, actual cu ft/sec
$Q_g$ = Gas flow rate, MMscfd
$Re$ = Reynolds number
$SG$ = Specific gravity
$T$ = Operating temperature, °F.
$U_d$ = Droplet settling velocity, fps
$V_g$ = Average gas velocity, fps
$V_t$ = Terminal settling velocity, fps
$V$ = Droplet velocity relative to the gas, fps
$Z$ = Gas compressibility factor
$\Delta SG$ = Difference in specific gravity
$\mu$ = Viscosity, cp
$\rho_l$ = Liquid density, lb/cu ft
$\rho_g$ = Gas density, lb/cu ft

For spherical droplets, the volume is

$$\frac{4}{3}\pi\left(\frac{D}{2}\right)^3 \text{ so that}$$

$$F_B = (\rho_l - \rho_g)\frac{\pi D^3}{6} \quad (2)$$

# understanding separator-sizing correlations

Fig. 2

Separators—Comparison 1

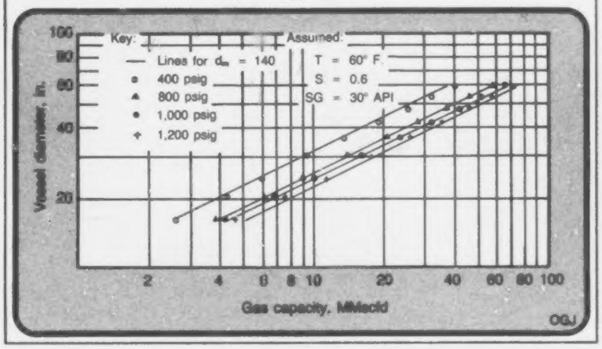
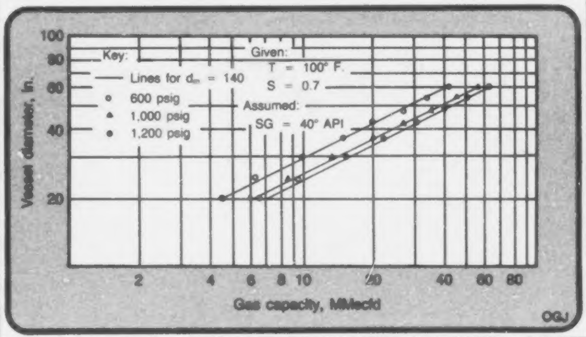


Fig. 3

Scrubbers—Comparison 2



The drag force depends on droplet cross-sectional area, gas viscosity and density, and droplet velocity relative to the gas:

$$F_D = C_D A_d \rho_g \frac{V^2}{2g} \qquad (3)$$

$C_D$ is the drag coefficient. Drag coefficients for spherical droplets depend on the Reynolds number for flow around the droplet. One correlation gives the drag coefficient as:

$$C_D = \frac{24}{Re} + \frac{3}{Re^{1/2}} + 0.34 \qquad (4)$$

Stoke's Law applies to low Reynolds numbers Re < 10 where the last two terms of Equation 4 can be neglected. Substituting $C_D = 24/Re$ in Equation 3, setting Equations 2 and 3 equal to each other, and making unit conversions, it is possible to write Stoke's Law as:

$$V_t = \frac{1.78 \times 10^{-6}\, (\Delta S.G.)\, d_m^{\,2}}{\mu} \qquad (5)$$

## Example problem

Given: MW = 29 P = 1,000 psia T = 560° R.
$d_m$ = 100 microns $(SG)_o$ = 1.0 $\mu$ = 0.0127 cp
Z = 1.0

$$\rho_g\ (\text{air}) = 4.83\ \frac{\text{lb}}{\text{ft}^3}$$

$$(SG)_g = \frac{4.83}{62.4} = 0.08 \text{ (relative to water)}$$

1. **Assume Stoke's Law governs**

$$V_{Stokes} = \frac{1.78 \times 10^{-6}\,(1 - 0.08)(100)^2}{0.0127} = 1.29 \text{ fps}$$

$$Re = 0.0049\ \frac{(4.83)(100)(1.29)}{0.0127} = 240$$

Re > 10 Stoke's Law does not apply

2. **Assume Newton's Law governs**

$$V_{Newton} = 0.0204 \left[\frac{(62.4 - 4.83)(100)}{4.83}\right]^{1/2} = 0.704 \text{ fps}$$

$$Re = 0.0049\ \frac{(4.83)(100)(0.704)}{0.0127} = 131$$

Re < 10,000 Newton's Law does not apply either.

Newton's Law applies to high Reynolds number flow ($Re > 10^4$). It neglects the first two terms in Equation 4 and states that $C_D$ is independent of Re and can be expressed as a constant.

Using this relationship it is possible to solve for terminal velocity as:

Fig. 4

Separators—Comparison 3

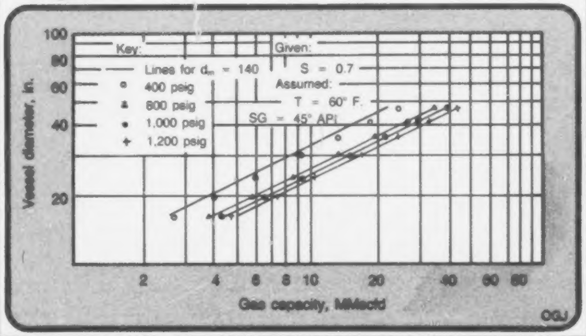


Fig. 5

Scrubbers—Comparison 4

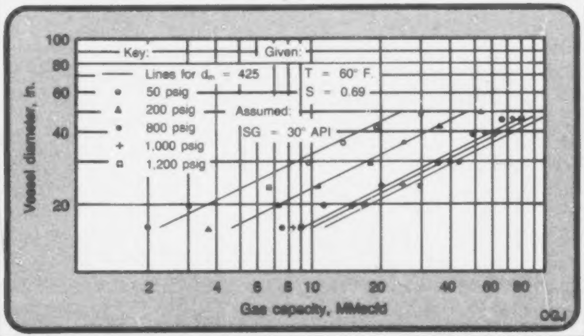


Fig. 6

## Separators—Comparison 5

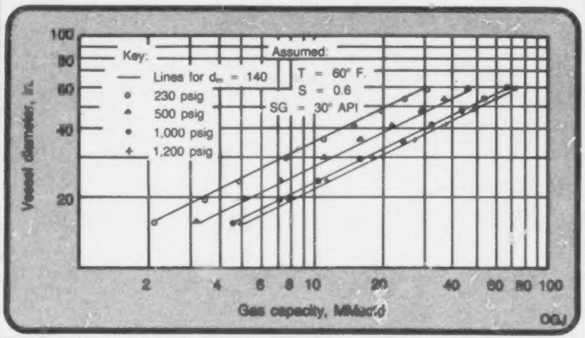
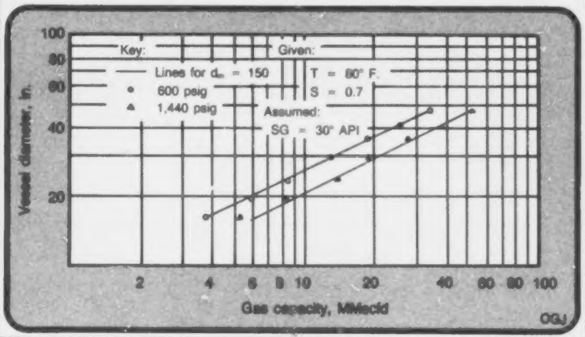


Fig. 7

## Separators—Comparison 6



$$V_t = 0.0119 \left[\left(\frac{\rho_l - \rho_g}{\rho_g}\right)\frac{d_m}{C_D}\right]^{1/2} \qquad (6)$$

If $C_D = 0.34$, Equation 6 can be written

$$V_t = 0.0204 \left[\left(\frac{\rho_l - \rho_g}{\rho_g}\right) d_m\right]^{1/2} \qquad (7)$$

For most gas-liquid separation problems in product facilities it can be shown that neither of these extremes is valid and the more complete formulation for $C_D$ in Equation 4 must be used.

The accompanying box presents an example showing this problem. Luckily, in the era of programmable calculators and personal computers it is easy to solve Equation 4 using an iterative solution by assuming a value for $C_D$, calculating $V_t$ from Equation 7, calculating Re from Equation 5, and then solving for $C_D$ from Equation 4.

Once $C_D$ is known, it is possible to use our model to derive a relationship for the diameter of the vessel. This is done by setting $V_t$ equal to the bulk upward flowing gas velocity. The minimum vessel diameter required to assure a slow enough gas velocity to settle a given size liquid droplet is:

$$d^2 = 5040 \frac{Q_g\, T\, Z}{P}\left[\left(\frac{\rho_g}{\rho_l - \rho_g}\right)\frac{C_D}{d_m}\right]^{1/2} \qquad (8)$$

Table 1

## Separator capacities*

| Vessel diameter, in. | Gas capacity, MMscfd at 400, psig | at 800 psig | at 1,000, psig | at 1,200 psig |
|---|---|---|---|---|
| 16 | 2.7 | 3.8 | 4.3 | 4.7 |
| 20 | 4.0 | 5.8 | 6.5 | 7.2 |
| 24 | 6.0 | 8.6 | 9.7 | 10.7 |
| 30 | 9.5 | 13.6 | 15.4 | 17.0 |
| 36 | 13.5 | 19.3 | 21.8 | 24.0 |
| 42 | 18.5 | 26.5 | 30.0 | 32.9 |
| 48 | 24.2 | 34.6 | 39.1 | 43.1 |

*Source: Smith Industries Inc.

It should be pointed out that Equation 8 is not based on Stoke's Law. It is a general equation that applies with any correlation for $C_D$, and we will routinely apply it outside the range of Reynolds numbers covered by Stoke's Law.

Also, our simple mathematical model assumed that no coalescence of droplets occurs in the separators. That is, it is possible to separate droplets smaller than $d_m$ if there is a mechanism in the separator which causes coalesence of these smaller droplets so that they grow to a diameter of $d_m$ or larger before exiting the top of the separator.

For a more complete derivation of the above equations and description of their use, see "Surface Production Operations" by K.E. Arnold and M.S. Stewart.[1]

### Scrubber correlations

Equation 8 was compared to separator and scrubber data from various design manuals and catalogs:

- *Comparison 1*—The Sivalls "Separator Design Manual"[2] states that separator gas handling capacities are based on Stoke's Law and are given by:

$$d^2 = 60 \frac{QZT}{PK}\left[\frac{\rho_g}{\rho_l - \rho_g}\right]^{1/2} \qquad (9)$$

Fig. 8

## Model of trayed tower

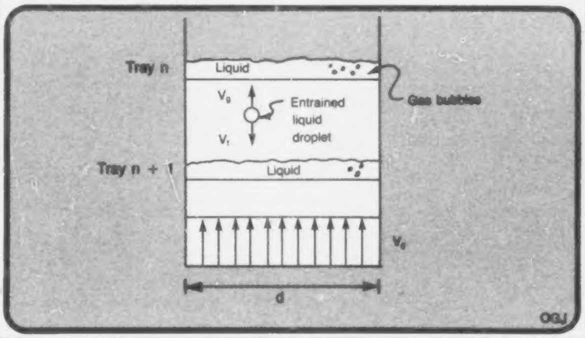


Fig. 9

## Trayed glycol towers—Comparison A

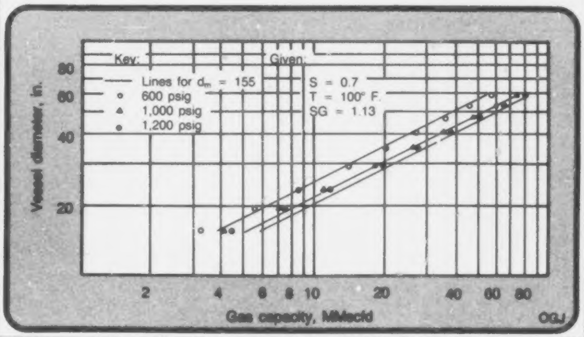


Fig. 10

Trayed glycol towers—Comparison B

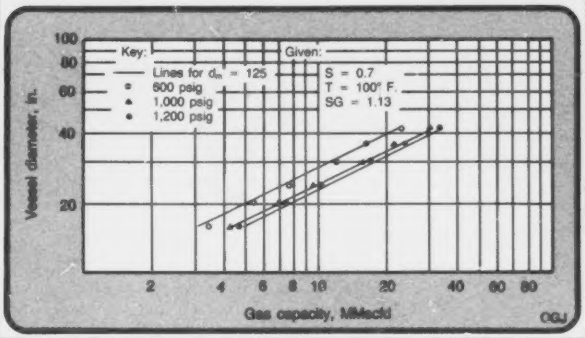


Fig. 11

Trayed glycol towers—Comparison C

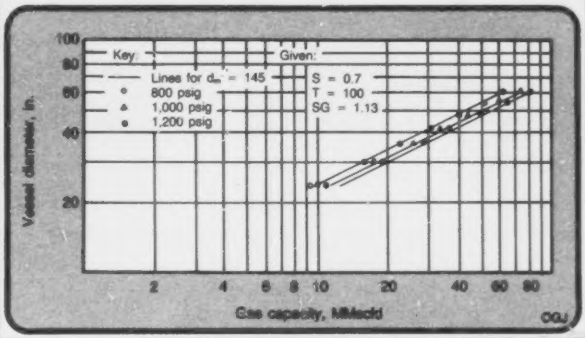


Table 2

## Scrubber capacities*

| Vessel diameter, in. | | | Gas capacity, MMscfd | | |
|---|---|---|---|---|---|
| | at 50, psig | at 200, psig | at 800, psig | at 1,000 psig | at 1,200 psig |
| 16 | 2.0 | 3.7 | 7.6 | 8.5 | 9.1 |
| 20 | 3.0 | 7.3 | 11.6 | 15.4 | 17.1 |
| 24 | 6.8 | 10.8 | 20.6 | 25.0 | 29.1 |
| 30 | 9.9 | 17.9 | 35.4 | 39.5 | 43.1 |
| 37 | 13.8 | 25.1 | | | |
| 39.5 | | | 49.6 | 55.6 | 60.6 |
| 43 | 19.4 | 35.6 | | | |
| 46 | | | 66.0 | 72.9 | 79.7 |
| 49 | 29.3 | 52.7 | | | |

*Source: Smith Industries Inc.

The similarities between this and Equation 8 are obvious. It can be shown that Equations 8 and 9 are identical if K equals 0.012 $[d_m/C_D]^{1/2}$.

The data plotted on Fig. 2 are based on the Sivalls design manual while the lines were generated by Equation 8 in the text (subsequent comparisons are presented in a similar fashion).

It can seen that our model matches the Sivalls data if we assumed a $d_m$ of 140 microns.

- *Comparison 2*—Sivalls Inc. quotes capacities for inlet scrubbers in literature on glycol dehydration systems. At first glance these appear to be different than the capacities given for similar-sized separators. However, once a correction is made for the different temperature and gravity assumed in the Sivalls capacity charts, Fig. 3 shows that a droplet size of 140 microns is still being used.
- *Comparison 3*—Table 1 shows capacities for various separators from the Smith Industries "Design Manual."[3] Fig. 4 compares these values to those obtained by Equation 8. It can be seen that the Smith sizing can be approximated by using a droplet settling size of 140 microns in our equation.
- *Comparison 4*—Smith Industries also quotes capacities for various vertical scrubbers as shown in Table 2.

The gas capacities of the scrubbers are much higher than separators. The scrubbers are designed to process a gas stream with small amounts of condensed liquids. Therefore, larger-diameter droplets may be allowed to pass through the gravity settling section to the mist extractor. Fig. 5 compares Smith Industries' capacities with results from Equation 8 using a droplet diameter of 425 microns.

- *Comparison 5*—Capacities for vertical separators from C.E. Natco catalog data are compared to Equation 8 in Fig. 6, which indicates a droplet size of 140 microns will duplicate these data.
- *Comparison 6*—Capacities for vertical separators from Black, Sivalls & Bryson Inc. (BS&B) catalog data. These are compared to Equation 8 in Fig. 7. A droplet diameter of 150 microns is applied.
- *Equation comparison*—American Petroleum Industry Recommended Practice RP 521 proposes the following equation for determining the dropout velocity or terminal settling velocity of a liquid droplet.

$$U_d = 1.15 \left[\frac{gD\,(\rho_l - \rho_g)}{\rho_g\, C}\right]^{1/2} \qquad (10)$$

This equation has the same form as Equation 6. API recommends using a droplet size between 300 and 600

Fig. 12

Trayed glycol towers—Comparison D

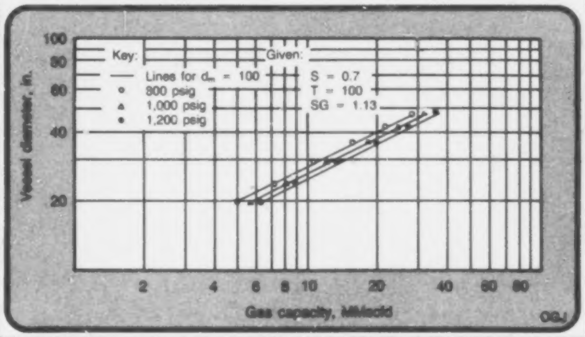
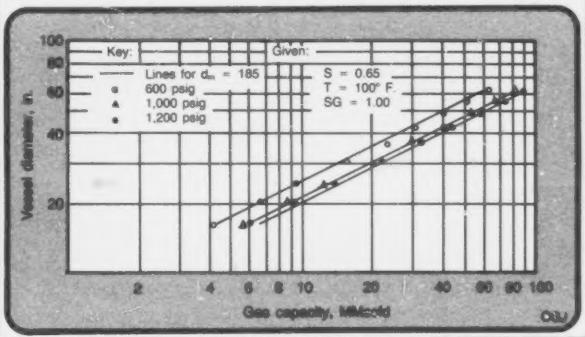
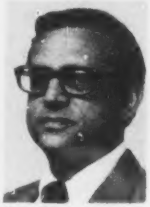


Fig. 13

Amine Contactors—Comparison



## The authors...



**Arnold**

**Sikes**

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Arnold has co-authored a textbook on surface facilities for oil fields.

Carl Sikes is a project/process engineer for Paragon Engineering Services, Houston, and has designed several product facility and gas plant projects for the Gulf Coast.

Sikes has a BS degree in chemical engineering from Texas A&M University. He is the primary author of the Two Phase Separation, Three Phase Separation and Oil Treating design guidelines in Paragon's "Production Facility Design Guideline and PC software" series and is currently revising the guidelines on produced water treating and oil desalting.

microns for flare scrubbers.

This application is similar to the Smith definition of a "scrubber."

That is, it represents a vessel which typically handles a small amount of liquid.

**Conclusions for separator sizing.** An inspection of Figs. 2 to 7 shows that most popular correlations for gas capacity of vertical separators are actually based on an approximation for settling 140 to 150 micron droplets from the gas phase. These correlations were justified at a time when it was difficult to use an iterative solution for $C_D$ and at a time when the consequences for incorrect sizing were less severe than they are in today's economic environment.

The correlations for "gas scrubbers" as opposed to separators appear to be based on 400 to 500 micron separation.

This is because most gas scrubbers are located downstream of separators where the bulk of the liquid has been removed.

Thus, they require less bulk separation of liquids prior to the mist extractor than would be the case for a separator on a true two-phase stream.

## Trayed tower correlations

Fig. 8 shows the mechanism occurring in a trayed tower. The gas bubbles up through trays or bubble caps passing through a layer of liquid creating a froth. The liquid droplets entrained in the gas must fall countercurrent to the upward flowing gas in the space between the trays.

One condition for proper tower design is to assure that there is adequate separation of the liquid drops from the gas so that the gas does not transport the liquid upward from tray to tray.

This then reduces to the same model we had for a separator. The diameter of the liquid droplet we wish to separate in the gas space above each tray sets a maximum gas velocity and thus a minimum tower diameter.

Following are some comparisons for Equation 8 in glycol contact tower sizing.

- *Comparison A*—Fig. 9 shows the capacity of trayed glycol contact towers as reported by Sivalls in its catalog for a 0.7 specific gravity gas and for pressures of 600, 1,000, and 1,200 psig. It can be seen that these data are nearly identical with the lines drawn using 155 micron separation and Equation 8.
- *Comparisons B,C,D*—Fig. 10 shows similar data for Smith Industries;[3] Fig. 11 for C.E. Natco, and Fig. 12 for BS&B.

All these sizing data are similar and indicate a sizing parameter of between 100 and 150 microns for trayed towers, which seems to be consistent with vendors' experience.

Droplet settling theory allows these data to be extrapolated to other conditions of gas properties, pressures, temperatures, etc., which are not available in vendors' published data.

For these common separators, most manufacturers use basically the same internals in their designs. The small difference in their choice of design droplet diameter probably reflects differences in approach to design-capacity safety factors. These decisions should be made by the project engineer because only he or she has the data to appropriately judge the cost and rewards of predicted vs. actual capacity requirements.

**Amine contact towers.** Fig. 13 shows Sivalls Inc. published data for amine units. It can be seen that these generally correspond to using Equation 8 with droplet diameter of 185 microns.

**Design sizes.** The analysis presented in this article seems to justify the following design droplet sizes: For separation of liquid from gas in a vertical separator at high liquid rate, the design diameter, in microns, should be 140-150; for low liquid rate, 400-500; for a glycol contactor 125-150; an amine contactor, 185.

**References**

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7. Sivalls, C.R., Glycol Dehydration Design Manual, Revision 9, Sivalls, Inc., Odessa, Tex., 1982.
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# Measurement of tank-bottom deformation reduces volume errors

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When liquids are added or removed from storage tanks, the tank bottom plate experiences elastic deformation caused by the changing load. This deformation results in tank volume inaccuracies not currently accounted for in tank calibrations.

Field evaluations show that the deformation can cause the tank volume to vary by as much as 0.1% from empty to full. This additional volume contributes to custody transfer understatements in both gauged receipts and sales that can result in losses to refiners, terminal operators, or transporters.

Here are some measuring techniques and analytical procedures to measure the amount of volume change caused by elastic deformation that will reduce the volume errors.

**Background.** Whenever a shore tank is filled, the tank bottom plate is subject to substantial loads. After a certain length of time, the periodic loads can cause both permanent and temporary elastic deformations of the bottom plate.

The permanent deformation (or settlement) is of structural concern, but does not cause errors in gauged custody transfers. On the other hand, elastic deformation occurs each time the tank is filled, and then, when emptied, the bottom plate reverts to its original position.

The current American Petroleum Institute (API) and American Society for Testing and Materials (ASTM) tank calibration standards do not include the effects of bottom plate deformation in the development of the tank capacity tables. Hence, if the bottom plate deformation is relatively large for a given tank, a significant error can occur everytime the tank gauge is converted into volume.

The error would tend to understate both gauged receipts and sales.

The elastic deformation of the bottom plate can vary from tank to tank and site to site depending on structural stiffness, soil conditions, nature of landfill, and soil compaction.

In initial attempts to measure the elastic deformation, a known water heel or level was established within the tank.

Deviations in the total water level for incremental loadings were used to test for the existence of bottom plate deformation. This method was prone to errors and gross inaccuracies due to measurement errors associated with water cuts, sampling, and laboratory analysis.

An alternate approach can be used that offers dramatically improved accuracy over the previous method. The alternative approach is based on maintaining a reference water level on the tank roof.

The procedure is primarily for establishing the bottom profile of an external floating roof tank, and it can be applied without having to take the tank out of service. Because the procedure utilizes existing roof holes for measurement locations, it is not possible to test fixed roof tanks without substantial modifications.

Fig. 1

Deformation determined from top

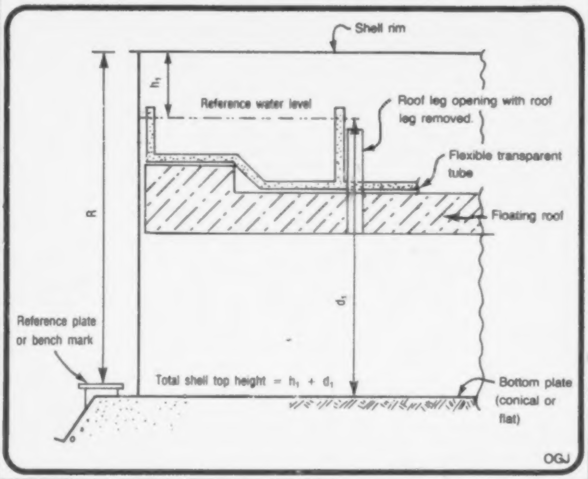
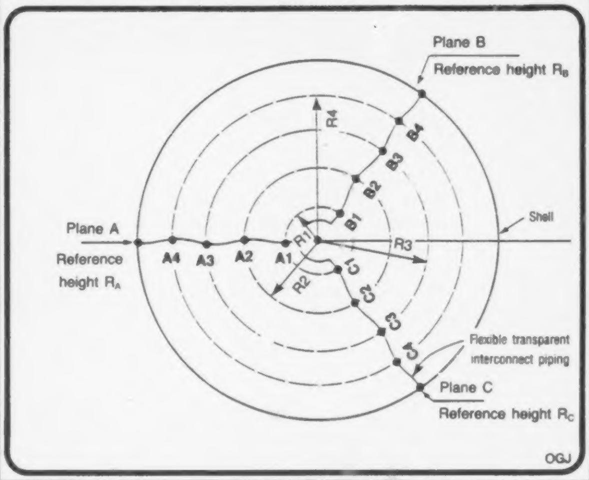

Shell rim
R
$h_1$
Reference water level
Roof leg opening with roof leg removed.
Flexible transparent tube
Floating roof
$d_1$
Reference plate or bench mark
Total shell top height = $h_1 + d_1$
Bottom plate (conical or flat)
OGJ

Fig. 2

Measurements made at 12 locations



Therefore, in those cases where tank characteristics and soil conditions are similar, it is suggested that the average bottom plate deformation value, determined from nearby or adjoining floating roof tanks, be used to estimate the effect on fixed roof tanks.

**Measurement and procedure.** The procedure involves establishing a reference water level on the floating roof top using a transparent piping arrangement as illustrated in Fig. 1. At any given liquid level in the tank, the height of the shell top ($h_1$), the depth to the bottom plate ($d_1$) from the reference water level, and the reference height (R) are measured.

Fig. 2 illustrates the plan view of an example three-plane (four test points per plane) piping arrangement spanning the cross-sectional area of the bottom plate. The roof legs are removed from these 12 radial locations to access the tank bottom.

The field measurements $h_1$, $d_1$, and R are undertaken in all three places and at the 12 radial locations. The measurements are then repeated at various liquid levels to determine incremental bottom deformation values.

**Analytical evaluation.** From field measurements, the total height to the shell top (i.e., $H_1 + d_1$) is computed at each radial location. For a given radial plane and at any given liquid fill height, the dimensions $h_1$ and R remain the same for all four radial locations in that plane (e.g., A1, A2, A3, and A4 in Fig. 2).

The bottom plate deformation for a given liquid level at a specific radial location is simply $\Delta(h_1 + d_1) \pm \Delta R$ where $\Delta(h_1 + d_1)$ is the deviation in the total shell top height and $\Delta R$ the variation in the external reference height between empty and a given liquid fill conditions. The above computation may be carried out for incremental fill heights from an empty tank to maximum fill conditions.

At radius (R1) the bottom plate deformation is the average of the three values (i.e., deformations at A1, B1, and C1 for radius R1). The bottom plate deformation profile may then be plotted for various fill heights as illustrated in Fig. 3. The volume of the deformation is computed using the profile geometry and the average tank diameter.

In those cases where deformation data are dimensionally very small, it is possible that they may be masked by measurement imprecision and, therefore, may be misinterpreted as bottom plate deformation. In order to establish that the deviations are indeed real and not a chance occurrance, the deformation data can be tested for statistical significance using statistical techniques. ased on the statistical analysis of the test data, it was concluded that the two-sigma (± 2) precision of the each test point is around 7 mm, or ¼ in. This precision level includes the combined effect of all random and systematic measurement errors and is considered reasonable for the field measurement technique.

**Results of field tests.** The measured bottom plate profile for full and empty conditions for two flat bottom tanks (Tanks 1 and 2), each 42 m in diameter, are presented in Fig. 3. Bottom plate deformation accounted for 0.08% of the total tank volume for Tank 1 and 0.12% for Tank 2.

These and other field tests have demonstrated that bottom plate deformation is a common phenomenon and that the results are often in the range of 0.1% understatement in gauged receipts and sales. Tests conducted on cone-down bottoms have demonstrated similar results with additional volumes as much as 0.1% being accounted for due to bottom plate deformation.

**Impact on oil loss.** The overall impact of tank bottom plate deformation on refinery mass balance (i.e., inputs less outputs) can be evaluated after testing both crude receipt tanks and product sales tanks. The impact on refinery oil loss can be accounted for by calculating the additional quantity due to bottom plate deformation in both the gauged crude receipt and product sales tanks. It is estimated that the impact on refinery oil loss may be a loss or gain of as much as 0.1% on input. Also, the deformation volume can cause distortions in transportation losses/gains, as well as month-end inventory.

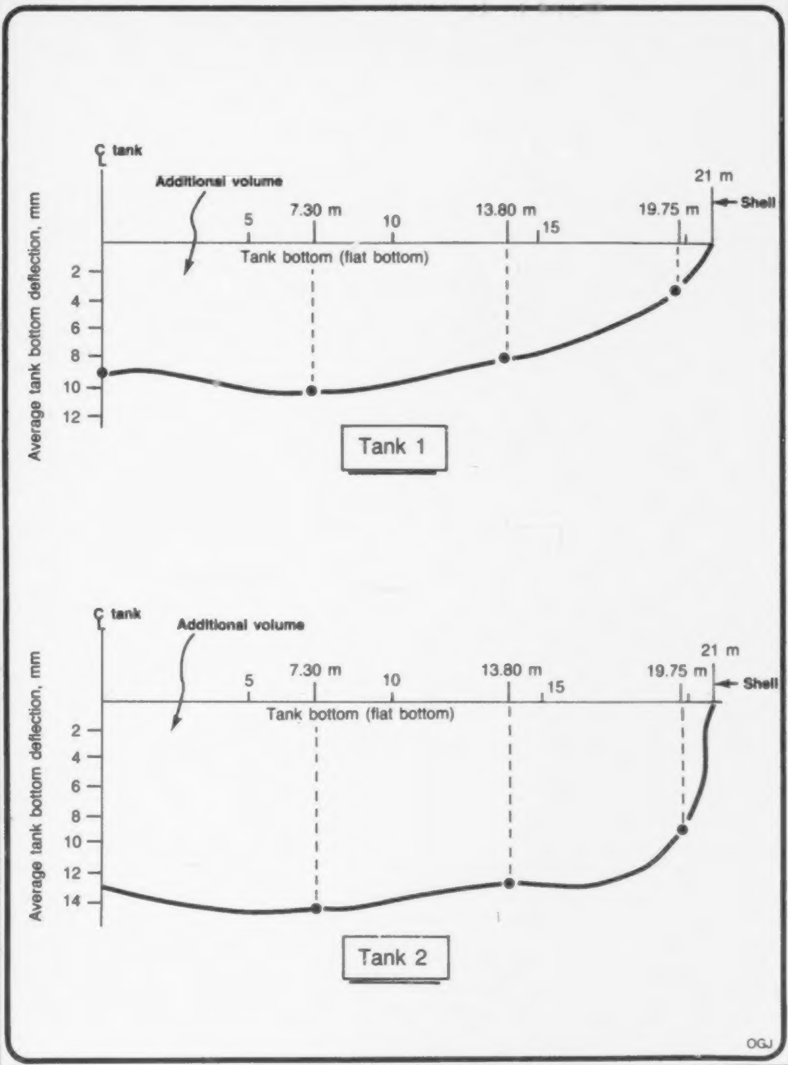
Using the procedures and the calculation techniques presented, it has been conclusively established that the bottom plate deformation could substantially impact tank volume determination. In addition, the reference water level method can be used to establish the "permanent" bottom plate profile at zero load or empty condition. Significantly, all field measurements can be made without taking the tank out of service.

At this time it is recommended that any bottom plate deformation in the custody transfer tanks should only be used for internal accounting as an oil loss reconciliation item. No adustments to the strapping tables, either directly or in the form of a correction factor, should be made until the testing and calculation procedures for bottom plate deformation are incorporated in API/International Standards Organization (ISO) calibrated standards.

The authors are currently working

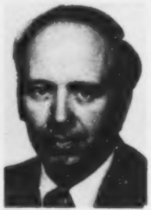
Fig. 3

## Two deformation profiles



## The authors...

**Sivaraman**



**Thorpe**

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with API/ISO tank calibration work groups to address this question to develop specific guidelines to include the impact of tank bottom plate deformation on tank volume.

**Acknowledgment.** The authors acknowledge the cooperation and assistance of Exxon affiliates around the world in conducting field tests and supplying the necessary manpower for the tests. ▪

# Model predicts alky unit acid consumption, additive effectiveness

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A statistical model has been developed to predict the acid consumption of a sulfuric acid alkylation unit. The model can also be used to determine the effectivensss of chemical additives.

An extended commercial-scale field trial of the model was run at Lyondell Petrochemical Co., Channelview, Tex., on an alkylation unit with and without additive treatment.

The complexities of a commercial alkylation process suggested the advantages of statistical modeling. Once it was decided that an acid-consumption model would help predict the effectiveness of such additives in alkylation reactions, it was necessary to establish which variable or variables were important in determining acid consumption.

Among the parameters to be considered were:

- Isobutane-to-olefin ratio in the feed
- Acid-to-hydrocarbon ratio
- Reaction temperature
- Acid concentration
- Rate of agitation
- Residence time
- Amount of inert reactants in feed

**Model development.** Lyondell Petrochemical's alkylation unit employed in this study was an effluent-refrigerated, sulfuric-acid alkylation unit (Fig. 1) having Stratco-designed horizontal contactors (Fig. 2) and a design capacity of 9,000 b/d.

All possible unit variables, which included 21 operational and 7 calculated variables, were considered as the basis on which to build an acid-consumption model.

The variables considered are shown in Table 1. In determining the size of the sample, the minimum number of sets of data required to build a statistically significant model would be n + 1 where n = 28. In all, 32 days of continuous data were collected.

Once the trial began, two variables—water content of the feed and sulfur content of the feed— subsequently had to be deleted from consideration.[2] Our method of analysis of water content of the feed was demonstrated to be unreliable at low concentrations. We determined that the relative humidity of the environment where sampling occurred interfered with the performance of the portable meter used.

We eliminated sulfur from our model because we saw that concentrations below 30 ppm in the feed did not appear to significantly affect the performance of the unit. The mean sulfur concentration during the collection of the base case data was 19.2 ppm.

The unit's operating temperature was measured at four different locations during the trial. After review, the experimental error observed when the numbers were summed and averaged was very small. As a result, this number was employed, and four additional variables were condensed into one.

The object of our model fitting was to obtain the simplest model that adequately fit the data.

Fig. 1

Effluent refrigerated $H_2SO_4$ alkylation

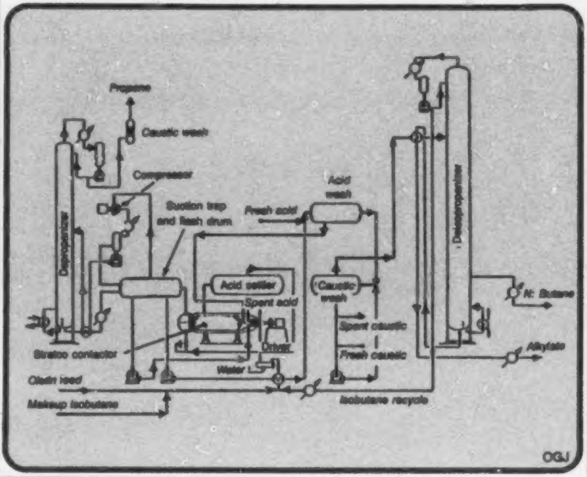
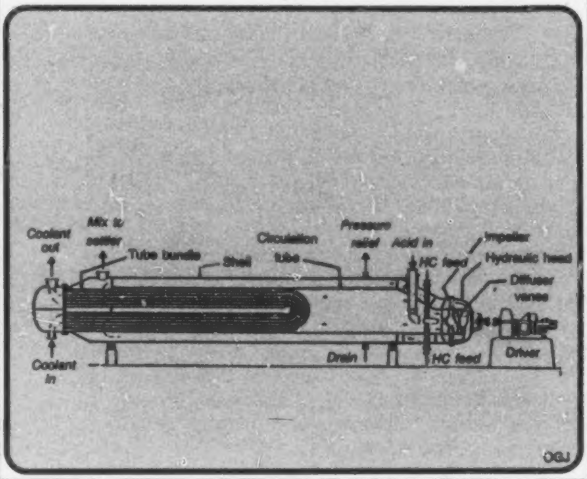

Propane
Caustic wash
Compressor
Depropanizer
Suction trap and flash drum
Fresh acid
Acid wash
Deisobutanizer
Acid settler
Spent acid
Caustic wash
N. Butane
Spent caustic
Fresh caustic
Stratco contactor
Driver
Water
Alkylate
Olefin feed
Makeup isobutane
Isobutane recycle
OGJ

Fig. 2

Stratco horiz. alkylation contactor


Coolant out
Mix to settler
Tube bundle
Shell
Circulation tube
Pressure relief
Acid in
HC feed
Impeller
Hydraulic head
Diffuser vanes
Drain
HC feed
Driver
Coolant in
OGJ

Therefore, as the dependent variable, we selected the pounds of acid consumed per gallon of alkylate produced (LBAGALK). Two approaches were used to select the subset of possible independent variables:

- Backward elimination. A stepdown procedure wherein the model first included all possible independent variables, and the variables were eliminated one by one as it was determined that they contributed little to the model.
- Stepwise regression. A procedure in which the model was built by adding one independent variable at a time and measuring its contribution to the model.[3]

We discovered the following independent variables most significantly affected the dependent variable, LBAGALK:

- DILUE—The amount of nonalkylate (inerts) compounds in the feed (e.g., n-propane, n-butane, n-pentane).
- AVTEMP—The average of four measured temperatures across the unit.
- EXTRAT—The external isobutane-to-olefin ratio, as calculated by the following equation (see Table 1 for an explanation of the variables used in the equation):

$$\text{EXTRAT} = ((\text{ICFD} * 100) + (\text{TOTFD}*\%\text{IC4}) + ((\text{TOTFRIG} - \text{EFRIG})* \text{IC4FRIG}) + (\text{T4O2OH}* \text{IC4TOH}))/(\text{TOTFD}* (\text{C3} + \text{B1} + \text{tB2} + \text{cB2}))$$

- DESIGN—The percent design that the unit was achieving during the base case, e.g., b/d alkylate produced/b/d design, %
- YIELD—A ratio of the alkylate product produced (APROD) to the volume of olefins fed to the unit, as calculated by the following equation:

$$\text{YIELD} = \text{APROD}/(\text{TOTFD}*0.343*(C_3 + \text{B1} + \text{tB2} + \text{cB2}))$$

- SPENT, the spent-acid concentration, wt %
- BD, the butadiene concentration in the feed, %
- C5, the $C_5+$ in the olefin charged, %
- FRESH, the fresh acid concentration, wt %

The next step required taking the data and reducing them to an equation consisting of a dependent variable, LBAGALK, and k independent variables, where k = 9.

The least-squares regression equation:

$$y = a + b_1X_1 + \cdots + b_9X_9$$

Fig. 3

Lyondell acid consumption

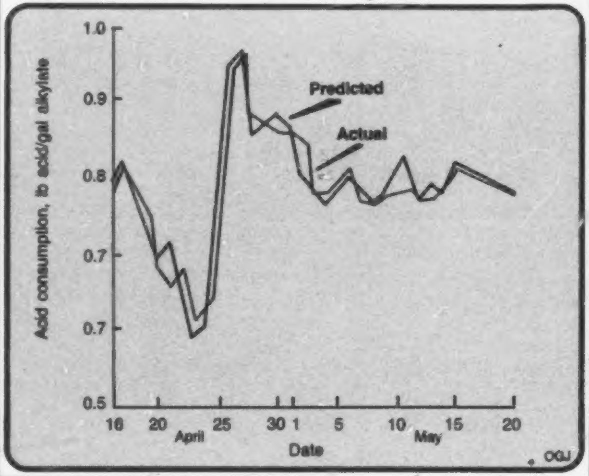
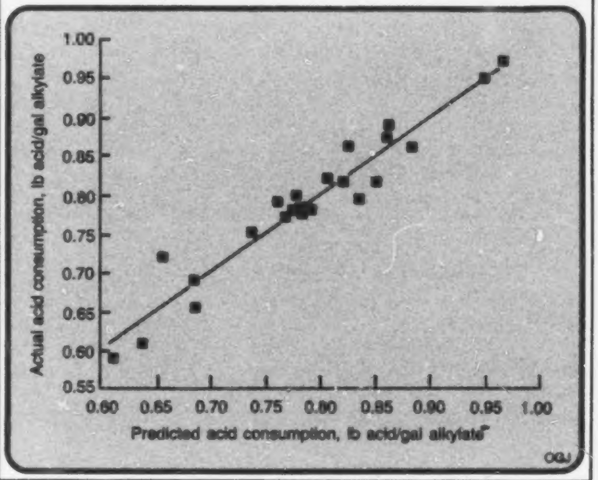


Fig. 4

Actual vs. predicted acid consumption



was solved by computing the augmented matrix of the sum of the squares and crossproducts and transforming these by row operations to yield estimates of the partial regression coefficients.[4]

To accomplish this complex task, we used a general linear multiple regression analysis program (GLM) available from SAS Institute Inc., Cary, N.C. We used the P (predict) option to predict the value of the dependent variable.

Comparing it to the observed value of the dependent variable, LBAGALK, the calculated difference between each observation is reported as the residual.[4] Once analysis of the data was complete, six data points with residuals greater than 10% of the average acid consumption were deleted and the data analysis repeated. For the multiple regression model described, $R^2 = 0.931$, the F value = 24.15, and PR > F = 0.0001. A graphic representation of the observed and predicted values of the data is shown in Figs. 3 and 4.

Having developed the acid-consumption equation shown below, the effect of an alkylation additive on acid consumption could be determined.

$$\text{LBAGALK} = a + b_1\,\text{DILUE} + b_2\,\text{AVTEMP} + b_3\,\text{EXTRAT} + b_4\,\text{DESIGN} + b_5\,\text{YIELD} + b_6\,\text{SPENT} + b_7\,\text{Bd} + b_8 C_5 + b_9\,\text{FRESH}$$

## Plant trial

A proprietary alkylation additive was then added to the fresh acid feed to the commercial unit described at a concentration of 1,500 wt ppm for a period of 90 days. Process variables were recorded throughout the treatment program and are summarized in Table 2.

**Results and discussion.** As previously stated, the following variables were considered by many authors and researchers to be important in determining alkylate quality: isobutane-to-olefin ratio, acid-to-hydrocarbon ratio, temperature, acid concentrations, mixing, residence time, and the amount of inerts in the feed.[1] Therefore, it is not surprising that stepwise and backward elimination regression analyses supported isobutane-to-olefin ratio, temperature, acid concentrations, and amount of inerts in a feed while also selecting butadiene and $C_5+$ concentrations in the feed.

As noted earlier, the object of this model was to obtain the simplest method of fitting the data. Because acid volume in the reactor was unobtainable, the calculation of olefin space velocity or contact time was not possible.[5] In essence, however, DE-

Table 1

## Operational and calculated unit variables

| Variable | Unit of measure | Variable type* | Abbreviation used in model |
|---|---|---|---|
| Average fresh acid addition | lb | 1 | ACID |
| Alkylate-to-olefin ratio | — | 1 | YIELD |
| Alkylate production | b/d | 2 | APROD |
| Average fresh acid addition | gpm | 2 | AVERFD |
| Average temperature | °F. | 1 | AVTEMP |
| Average total feed | gpm | 2 | TOTFD |
| Butadiene in olefin charge | % | 2 | BD |
| 1-butene in olefin charge | % | 2 | B1 |
| Cis-2-butene in olefin charge | % | 2 | CB2 |
| Design | % | 1 | DESIGN |
| Deisobutanizer overheads | gpm | 2 | T402OH |
| Diluents in feed | % | 2 | DILUE |
| External isobutane-to-olefin ratio | — | 1 | EXTRAT |
| Fresh acid concentration | wt % | 2 | FRESH |
| Isobutane feed | [illegible] | 2 | ICFD |
| Isobutane in olefin charge | % | 2 | IC4 |
| Isobutane in deisobutanizer overheads | % | 2 | IC4TOH |
| Isobutane in refrigerant recycle | % | 2 | IC4FRIG |
| Octane number, (R + M)/2 | — | 1 | OCTANE |
| Pentanes and higher in olefin charge | % | 2 | C5 |
| Pounds acid/gallon alkylate | — | 1 | LBAGALK |
| Propylene in olefin charge | % | 2 | C3 |
| Refrigerant recycle | gpm | 2 | EFRIG |
| Temperature, E-402 exchanger | °F. | 2 | E402T |
| Temperature, E-403 exchanger | °F. | 2 | E403T |
| Temperature, E-404 exchanger | °F. | 2 | E404T |
| Temperature, E-405 exchanger | °F. | 2 | E405T |
| Total refrigerant recycle | gpm | 2 | TOTFRIG |
| Trans-2-butene in olefin charge | % | 2 | TB2 |
| Spent acid concentration | wt % | 2 | SPENT |
| Sulfur in olefin charge | ppm | 2 | PPMS |
| Water in olefin charge | ppm | 2 | H2O |

* 1 = Calculated value, 2 = Unit operation value

Table 2

## Alkylation unit variable names

| Variable | Label | Mean | Minimum value | Maximum value | Range |
|---|---|---|---|---|---|
| TOTFD | Avg. total feed, gpm | 354.24 | 326.30 | 398.80 | 72.50 |
| ICFD | Isobutane feed, gpm | 91.73 | 55.00 | 150.00 | 95.00 |
| AVFRFD | Avg. fresh acid addition, gpm | 17.12 | 12.13 | 19.58 | 7.45 |
| TOTFRIG | Total refrigerant recycle, gpm | 784.04 | 630.00 | 825.00 | 195.00 |
| T402OH | T-402 overhead, gpm | 919.38 | 852.00 | 963.00 | 111.00 |
| E402T | E-402 temp., °F. | 58.00 | 53.00 | 60.00 | 7.00 |
| E403T | E-403 temp., °F. | 58.35 | 53.00 | 60.00 | 7.00 |
| E404T | E-404 temp., °F. | 58.35 | 53.00 | 60.00 | 7.00 |
| E405T | E-405 temp., °F. | 58.38 | 53.00 | 60.00 | 7.00 |
| C3 | $C_3=$ IN olefin charge, % | 1.92 | 1.10 | 2.70 | 1.60 |
| IC4 | $IC_4$ in olefin charge, % | 33.54 | 27.40 | 37.00 | 9.60 |
| B1 | $B_1$ in olefin charge, % | 23.66 | 22.00 | 28.00 | 6.00 |
| TB2 | Trans $B_2$ in olefin charge, % | 12.53 | 7.10 | 13.70 | 6.60 |
| CB2 | Cis $B_2$ in olefin charge, % | 8.64 | 7.90 | 9.10 | 1.20 |
| BD | Butadiene in olefin charge, % | 0.26 | 0.20 | 0.36 | 0.16 |
| PPMS | Sulfur in olefin charge, ppm | 19.19 | 10.00 | 46.00 | 36.00 |
| IC4TOH | $IC_4$ in T-402 overhead, % | 79.70 | 73.10 | 84.30 | 11.20 |
| IC4FRIG | $IC_4$ in refrigerant recycle, % | 72.68 | 64.00 | 78.60 | 14.60 |
| SPENT | Spent acid concentration, wt % | 91.47 | 90.10 | 92.50 | 2.40 |
| APROD | Daily alky. production, b/d | 11,368.08 | 10,221.00 | 12,410.00 | 2,189.00 |
| EFRIG | E-404 refrigerant recycle, gpm | 288.77 | 184.00 | 360.00 | 176.00 |
| C5 | $C_5+$ in olefin charge, % | 0.89 | 0.00 | 1.70 | 1.70 |
| H2O | Moisture in olefin charge | 4,259.90 | 462.00 | 12,120.00 | 11,658.00 |
| FRESH | Fresh acid concentration, wt % | 99.43 | 99.10 | 99.80 | 0.70 |
| ACID | Avg. fresh acid addition × 523.35 | 8,962.37 | 6,348.24 | 10,247.19 | 3,898.96 |
| LBAGALK | lb acid/gal alkylate | 0.79 | 0.59 | 0.97 | 0.38 |
| DILUE | Diluents in feed, % | 19.71 | 16.90 | 22.80 | 5.90 |
| AVTEMP | Avg. contactor temp., °F. | 58.27 | 53.00 | 60.00 | 7.00 |
| EXTRAT | External I $C_4$/olefin ratio | 7.90 | 6.79 | 8.62 | 1.83 |
| DESIGN | Percent of design | 132.19 | 118.85 | 144.30 | 25.45 |
| YIELD | Alkylate/olefin ratio | 2.00 | 1.89 | 2.19 | 0.30 |

Table 3

## Lyondell Petrochemical acid consumption data

| Observation No. | Date | Model predicted | lb acid/gal alky. | Diff lb acid/gal alky | Reduction, % |
|---|---|---|---|---|---|
| 1 | 06/17/85 | 1.04337 | 0.85085 | 0.19252 | 18.452 |
| 2 | 06/18/85 | 1.05422 | 0.84348 | 0.21074 | 19.991 |
| 3 | 06/19/85 | 0.95925 | 0.90834 | 0.05091 | 5.308 |
| 4 | 06/21/85 | 1.04198 | 0.99444 | 0.04754 | 4.562 |
| 5 | 06/22/85 | 1.11441 | 0.98345 | 0.13096 | 11.752 |
| 6 | 06/23/85 | 0.97612 | 0.93024 | 0.04588 | 4.701 |
| 7 | 06/24/85 | 1.05424 | 0.85254 | 0.20170 | 19.132 |
| 8 | 06/25/85 | 1.05412 | 0.84439 | 0.20973 | 19.896 |
| 9 | 06/26/85 | 0.97199 | 0.86369 | 0.10830 | 11.142 |
| 10 | 06/28/85 | 0.91753 | 0.81571 | 0.10182 | 11.097 |
| 11 | 06/29/85 | 0.92621 | 0.80938 | 0.11683 | 12.614 |
| 12 | 06/30/85 | 1.00050 | 0.86725 | 0.13325 | 13.319 |
| 13 | 07/01/85 | 0.99399 | 0.90690 | 0.08709 | 8.762 |
| 14 | 07/02/85 | 1.09602 | 0.92061 | 0.17541 | 16.004 |
| 15 | 07/03/85 | 1.04983 | 0.83545 | 0.21438 | 20.420 |
| 16 | 07/04/85 | 1.07857 | 0.88367 | 0.19490 | 18.070 |
| 17 | 07/05/85 | 0.92221 | 0.82335 | 0.09886 | 10.720 |
| 18 | 07/06/85 | 0.90292 | 0.85691 | 0.04601 | 5.095 |
| 19 | 07/07/85 | 0.80067 | 0.79758 | 0.00309 | 0.386 |
| 20 | 07/11/85 | 0.91661 | 0.84952 | 0.06709 | 7.319 |
| 21 | 07/12/85 | 0.90665 | 0.80721 | 0.09944 | 10.968 |
| 22 | 07/13/85 | 0.81053 | 0.81364 | -0.00311 | - 0.384 |
| 23 | 07/14/85 | 0.86172 | 0.83651 | 0.02521 | 2.926 |
| 24 | 07/15/85 | 0.96683 | 0.91510 | 0.05173 | 5.350 |
| 25 | 07/16/85 | 0.85973 | 0.89714 | -0.03741 | - 4.352 |
| 26 | 07/17/85 | 0.77751 | 0.87540 | -0.09789 | -12.590 |
| 27 | 07/20/85 | 0.83669 | 0.96964 | -0.13295 | -15.890 |
| 28 | 07/21/85 | 0.90541 | 0.98830 | -0.08289 | - 9.155 |
| 29 | 07/22/85 | 1.02255 | 0.90233 | 0.12022 | 11.757 |
| 30 | 07/23/85 | 1.11355 | 0.94656 | 0.16699 | 14.996 |
| 31 | 07/24/85 | 1.08218 | 0.90932 | 0.17286 | 15.973 |
| 32 | 07/26/85 | 1.02904 | 0.94775 | 0.08129 | 7.899 |
| 33 | 07/27/85 | 0.88929 | 0.80504 | 0.08425 | 9.474 |
| 34 | 07/28/85 | 0.99633 | 0.82930 | 0.16703 | 16.765 |
| 35 | 07/29/85 | 0.94496 | 0.81836 | 0.12660 | 13.397 |
| 36 | 07/30/85 | 0.96953 | 0.84322 | 0.12631 | 13.027 |
| 37 | 07/31/85 | 0.99924 | 0.87629 | 0.12295 | 12.304 |
| 38 | 08/01/85 | 0.96321 | 0.87276 | 0.09045 | 9.390 |
| 39 | 08/02/85 | 1.18641 | 0.89444 | 0.29198 | 24.610 |
| 40 | 08/03/85 | 1.08240 | 0.84580 | 0.23660 | 21.859 |
| 41 | 08/04/85 | 1.14610 | 0.88025 | 0.26584 | 23.196 |
| 42 | 08/05/85 | 1.20726 | 0.87932 | 0.32794 | 27.164 |
| 43 | 08/06/85 | 1.12430 | 0.89005 | 0.23425 | 20.835 |
| 44 | 08/07/85 | 1.11464 | 0.86528 | 0.24936 | 22.372 |
| 45 | 08/08/85 | 1.07741 | 0.81869 | 0.25872 | 24.013 |
| 46 | 08/09/85 | 1.12186 | 0.87468 | 0.24718 | 22.033 |
| 47 | 08/10/85 | 1.16793 | 0.90052 | 0.26741 | 22.896 |
| 48 | 08/11/85 | 1.05887 | 0.90345 | 0.15542 | 14.678 |
| 49 | 08/12/85 | 1.00410 | 0.92166 | 0.08244 | 8.210 |
| 50 | 08/13/85 | 0.91781 | 0.84878 | 0.06903 | 7.521 |
| 51 | 08/14/85 | 1.00536 | 0.84765 | 0.15571 | 15.686 |
| 52 | 08/15/85 | 1.04693 | 0.91548 | 0.13144 | 12.555 |
| 53 | 08/16/85 | 1.09099 | 0.92812 | 0.16287 | 14.929 |
| 54 | 08/17/85 | 0.93535 | 0.81627 | 0.11908 | 12.731 |
| 55 | 08/18/85 | 1.01615 | 0.83538 | 0.18077 | 17.790 |
| 56 | 08/19/85 | 1.00488 | 0.78406 | 0.22081 | 21.974 |
| 57 | 08/20/85 | 0.99117 | 0.73159 | 0.25957 | 26.189 |
| 58 | 08/21/85 | 0.97335 | 0.74366 | 0.22968 | 23.597 |
| 59 | 08/22/85 | 0.98233 | 0.75036 | 0.23196 | 23.614 |
| 60 | 08/23/85 | 1.00797 | 0.76543 | 0.24254 | 24.062 |
| 61 | 08/24/85 | 1.01352 | 0.78961 | 0.22391 | 22.092 |
| 62 | 08/29/85 | 1.01873 | 1.05963 | -0.04090 | - 4.015 |
| 63 | 08/30/85 | 1.37402 | 1.11572 | 0.25830 | 18.799 |
| 64 | 08/31/85 | 1.02975 | 0.88497 | 0.14478 | 14.060 |
| 65 | 09/01/85 | 1.03264 | 0.87361 | 0.15903 | 15.400 |
| 66 | 09/05/85 | 1.06329 | 1.07289 | -0.00959 | - 0.902 |
| 67 | 09/06/85 | 1.11574 | 1.04163 | 0.07410 | 6.641 |
| 68 | 09/07/85 | 1.03671 | 0.84142 | 0.19529 | 18.837 |
| 69 | 09/08/85 | 1.02697 | 0.78644 | 0.24053 | 23.421 |
| 70 | 09/09/85 | 1.08402 | 0.75782 | 0.32620 | 30.092 |
| 71 | 09/10/85 | 0.99508 | 0.76294 | 0.23214 | 23.329 |
| 72 | 09/11/85 | 0.91484 | 0.78500 | 0.12983 | 14.192 |
| 73 | 09/12/85 | 0.88900 | 0.80050 | 0.08850 | 9.955 |
| 74 | 09/13/85 | 0.99903 | 0.85326 | 0.14576 | 14.590 |
| 75 | 09/14/85 | 1.02548 | 0.88201 | 0.14347 | 13.990 |
| 76 | 09/15/85 | 1.04153 | 0.89760 | 0.14392 | 13.818 |
| 77 | 09/16/85 | 1.11997 | 0.89760 | 0.22237 | 19.855 |
| 78 | 09/17/85 | 1.16539 | 0.93800 | 0.22739 | 19.512 |
| 79 | 09/18/85 | 1.20719 | 0.94000 | 0.26718 | 22.132 |
| 80 | 09/19/85 | 1.11600 | 0.93694 | 0.17905 | 16.044 |
| 81 | 09/20/85 | 1.06027 | 1.02176 | 0.03850 | 3.632 |
| 82 | 09/21/85 | 0.95304 | 0.97014 | -0.01709 | - 1.793 |
| 83 | 09/22/85 | 1.08458 | 0.85758 | 0.22700 | 20.929 |
| 84 | 09/23/85 | 1.17287 | 0.83151 | 0.34136 | 29.104 |
| 85 | 09/29/85 | 1.06850 | 0.78652 | 0.28197 | 26.390 |
| 86 | 09/30/85 | 1.01193 | 0.82904 | 0.18288 | 18.073 |
| 87 | 10/01/85 | 1.25378 | 0.83538 | 0.41840 | 33.371 |
| 88 | 10/02/85 | 1.08566 | 0.76805 | 0.31761 | 29.255 |
| 89 | 10/03/85 | 1.01478 | 0.82585 | 0.18893 | 18.618 |
| 90 | 10/04/85 | 1.09325 | 0.95799 | 0.13526 | 12.372 |
| 91 | 10/05/85 | 1.12797 | 0.90275 | 0.22521 | 19.966 |
|  | MEAN | 1.02 | 0.87 | 0.15 | 14.7 |

## The authors. . .

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**Miller**

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**Knickerbocker**

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SIGN is a measure of olefin space velocity or contact time because the unit is theoretically designed to handle some volume of olefin per hour or day.

If x times that volume is fed, it affects the olefin space velocity as shown below:

Unit design = 9,000 b/d
Actual average total feed (mean)
= 12,145 b/d
DESIGN = 12,145 b/d/9,000 b/d

= 1.35 (135%)
I/O ratio = 7.90
V acid in contactors = 0.5 × 8,900 gal = 4,450 gal
Theoretical average olefin feed = 1,011 b/d = 1,769.6 gal/hr
Actual average olefin feed = 1,364.6 b/d = 2,388 gal/hr
$(SV)_{OD} = (SV)_{O}$ at design $= 0.40\ hr^{-1}$
$(SV)_{OA} = (SV)_{O}$ actual $= 0.54\ hr^{-1}$
$(SV)_{OA}/(SV)_{OD} = 0.54\ hr^{-1}/0.40\ hr^{-1} = 1.34$

An acid-to-hydrocarbon ratio of 1:1 is assumed for the volume of acid in the contactors.

The ratio of olefin space velocity at design vs. the olefin space velocity under actual operating conditions approaches the value obtained for DESIGN. Thus, DESIGN becomes a reasonable means by which to approximate olefin space velocity.

The data obtained from the alkylation additive trial at Lyondell Petrochemical, shown in Table 3, display both model-predicted and actual pounds of acid consumed per gallon of alkylate produced—the difference between predicted and actual, and the percent reduction in acid consumption.

Positive differences are observed during the trial with the exception of Observation numbers 22, 25-28, 62, 66, and 82. The negative values obtained in Observations 22 and 66 were small and are considered reasonable considering the degree to which the model fit actual data.

The negative values obtained in observations 25-28 were well documented and were the result of additive pump problems experienced during the test. The negative values of observations 62 and 82 remain unexplained, possibly the result of an increase in the water or sulfur content of the feed which were not considered in the model.

The predicted value of LBAGALK during the test case was 1.02. The actual acid consumption value realized for the 90-day trial period was 0.87; a decrease of 0.15 lb of acid/gal of alkylate produced, or 14.7%.

During the test case, 5,923,937 lb of sulfuric acid were saved, at an overall cost savings of $281,387. The annual savings for this unit (net of additive costs) would be $667,112; an average acid savings to chemical cost ratio of 2.56:1.

The work suggests additive performance is dose related. We will attempt to better define the concentration range for which acid consumption is optimized. Further, because it has been reported that the use of the alkylation additive employed in this test has improved alkylate quality,[7] we will complete and report on additional definitive studies in this area.

Once optimized, the use of an alkylation additive would possibly allow a refiner to operate above design without consuming significantly larger amounts of acid, allow for better emulsion resolution decreasing the possibility of acid carry-over to recovery towers, and improve the octane value of the alkylate produced.

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# Titration method improves water measurement

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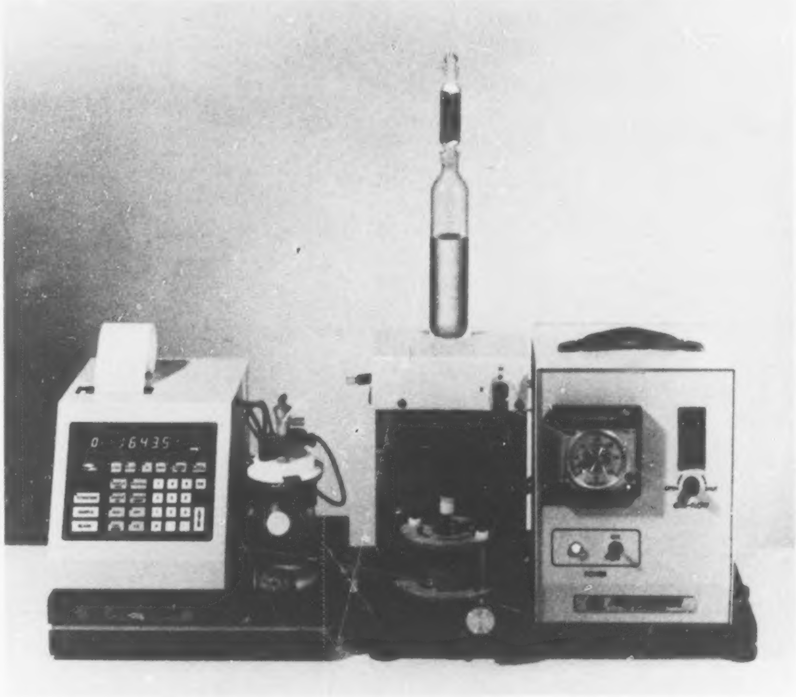
Water content in petroleum products and bituminous materials can be determined by a new method using a Coulometric Karl Fischer titrator.[1]

The method offers reduced analysis time and operator bias, and increased detection sensitivity and improved precision compared to the existing method jointly adopted as a standard by the American Society for Testing and Materials (ASTM), the American Petroleum Institute (API), and the Institute of Petroleum (IP).

Measurement is accurate, precise, rapid, and flexible when the titrator is used in conjunction with a liquid-evaporation accessory and pyridine-free Karl Fischer reagents.[2]

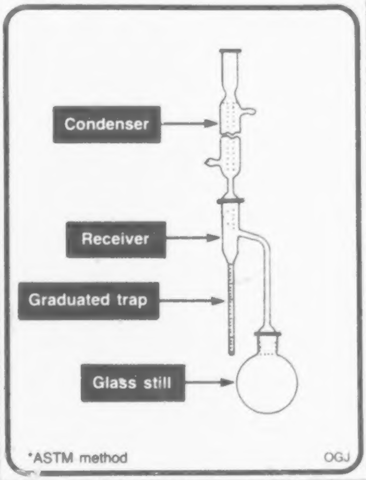
To validate the capability of the new method, a study was conducted to compare the existing standard method with the titration method. The study was conducted in a commercial, production-oriented laboratory, using a variety of recently obtained petroleum samples. Water content was determined for each sample by both methods, and the results were compared and statistically evaluated for correlation to the standard method, precision, detection sensitivity, and analysis time.



**Coulometric Karl Fischer titrator** and oil evaporation system used for the determination of water content in petroleum products (Fig. 2).

Fig. 1

Distillation assembly*



*ASTM method

OGJ

**Methods and materials.** The performance of the standard distillation procedure, ASTM D95-83, API MPMS Chapter 10.5, and IP 74/77, commonly called the Dean and Stark method, was in accordance with the specifications given in the ASTM publication.[3] The performance of the Karl Fischer/evaporation procedure was in accordance with the instruction manual supplied with the instrument.

Both procedures utilize the same extraction principle: The material to be tested is heated with a water-immiscible solvent which co-distills with the water in the sample. For this study, reagent-grade toluene was used as the common solvent.

Sample types were, in some cases, unknown but most were burner fuel oils ranging in grade from No. 2 to No. 6. All were petroleum products or bituminous materials.

Comparison analyses were performed on the same day to avoid moisture changes in the samples due to differences in storage time or changes in humidity. All distillation determinations were performed by a single operator, while all instrumental determinations were performed by a second, separate operator. Samples were well mixed before each determination by agitating and inverting the sample container several times.

The study was based on results for water content in 38 samples of petroleum products.

**Standard procedure.** In the ASTM procedure, condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and solvent returning to the still (Fig. 1).

The trap and contents are allowed to cool, and the volume of water is read to the nearest scale division (0.10 ml). Results are normally calculated as percent water on a volume/volume basis as follows:

$$\% \text{ water} = (V_1/V_2) \times 100$$

where:

$V_1$ = ml $H_2O$ collected
$V_2$ = ml sample used

For this study, 50 ml samples were used along with 100 ml of solvent and a 25-ml trap.

**Instrumental procedure.** Utilizing the Coulometric Karl Fischer titration/evaporation system (Fig. 2), the sample is added to the oil evaporation accessory where it mixes with approximately 10 ml of predried toluene in the evaporation chamber.

The sample dissolves in the solvent and, when heated to 110° C., forms an azeotropic mixture with the water in the sample. The mixture is heated to co-distill solvent and water in the sample.

Dry nitrogen gas, at a flow rate of 90 ml/min, carries the distillate vapor to the electrolytic cell of the Coulometric titrator where the moisture in the distillate is rapidly and easily quantified (Fig. 3).

The titrator automatically performs the titration and endpoint detection, and calculates the moisture content based on sample size and the number of Coulombs required to reach the reaction endpoint.

In the Karl Fischer method for water content by Coulometry,[4] the titration begins with the electrolytic oxidation of iodine ions shown in Equation 3, when the distillate vapor reaches the anode and cathode reagents in the titrator reaction cell:

$$ROH + SO_2 + R'N \rightleftharpoons [R'NH]\, SO_3 R \quad (1)$$

$$H_2O + I_2 + [R'NH]\, SO_3R + 2R'N \rightarrow [R'NH]\, SO_4R + 2[R'NH]I \quad (2)$$

$$2\, R'NH^+I^- + R'N \xrightarrow{-2e} R'N \cdot I_2 + 2R'NH^+ \quad (3)$$

The reaction is performed quantitatively with 100% electroytic efficiency, and the quantity of generated iodine is directly proportional to the quantity of electricity consumed. The generated iodine is used as the titration agent to force the reaction to the right. Iodine ions are generated simultaneously, recirculated, and reused.

Results are obtained from Faraday's Law by the integration of the quantity of electricity required to produce a reaction endpoint. From Equation 2, 1 mol of water is titrated with 1 mol of iodine which is generated by the two-electron reaction from Equation 3. Therefore, one mol of water is titrated by 2 Faradays (96487 × 2 Coulombs):

$$1\text{g } H_2O \text{ titrated by } 96{,}487 \times 2 \text{ Coulombs}/18.015 \text{ g } H_2O/\text{mol} = 10{,}712 \text{ Coulombs}$$

**Correlation.** Results of the study showed excellent agreement between both methods (correlation coefficient by linear regression of 0.9912). Fig. 4 illustrates that the results from Table 1 of 12 samples ranging from 0.13% to 2.54% $H_2O$, measured by the instrumental procedure, were slightly elevated when compared to results from

Table 1

## Moisture content measurement comparisons

| Sample no. | Instrumental results, % $H_2O$ | Distillation results, % $H_2O$ | Difference, % $H_2O$ | Instrumental time, min | Distillation time, min | Difference, min |
|---|---|---|---|---|---|---|
| 1 | 0.30 | 0.32 | −0.02 | 6 | 70 | 64 |
| 2 | 0.01 | 0.00 | +0.01 | 1 | 90 | 89 |
| 3 | 0.02 | 0.00 | +0.02 | 4 | 85 | 81 |
| 4 | 0.02 | 0.00 | +0.02 | 3 | 80 | 77 |
| 5 | 0.01 | 0.00 | +0.01 | 2 | 85 | 83 |
| 6 | 0.01 | 0.00 | +0.01 | 2 | 90 | 88 |
| 7 | 0.06 | 0.00 | +0.06 | 6 | 100 | 94 |
| 8 | 0.04 | 0.00 | +0.04 | 6 | 95 | 89 |
| 9 | 0.33 | 0.20 | +0.13 | 7 | 85 | 78 |
| 10 | 0.01 | 0.00 | +0.01 | 1 | 75 | 74 |
| 11 | 0.01 | 0.00 | +0.01 | 2 | 75 | 73 |
| 12 | 0.01 | 0.00 | +0.01 | 2 | 75 | 73 |
| 13 | 0.17 | 0.08 | +0.09 | 7 | 80 | 73 |
| 14 | 0.05 | 0.00 | +0.05 | 5 | 80 | 75 |
| 15 | 0.01 | 0.00 | +0.01 | 3 | 80 | 77 |
| 16 | 0.00 | 0.00 | 0.00 | 1 | 70 | 69 |
| 17 | 0.61 | 0.56 | +0.05 | 11 | 100 | 89 |
| 18 | 0.02 | 0.00 | +0.02 | 4 | 80 | 76 |
| 19 | 0.10 | 0.04 | +0.06 | 7 | 80 | 73 |
| 20 | 0.19 | 0.20 | −0.01 | 6 | 85 | 79 |
| 21 | 0.15 | 0.16 | −0.01 | 7 | 85 | 78 |
| 22 | 0.24 | 0.08 | +0.16 | 7 | 80 | 73 |
| 23 | 0.02 | 0.00 | +0.02 | 4 | 90 | 86 |
| 24 | 0.01 | 0.00 | +0.01 | 3 | 90 | 87 |
| 25 | 0.14 | 0.00 | +0.14 | 6 | 90 | 84 |
| 26 | 0.24 | 0.08 | +0.16 | 6 | 90 | 84 |
| 27 | 0.13 | 0.00 | +0.13 | 5 | 85 | 80 |
| 28 | 0.34 | 0.00 | +0.34 | 7 | 95 | 88 |
| 29 | 0.15 | 0.00 | +0.15 | 6 | 90 | 84 |
| 30 | 0.38 | 0.00 | +0.38 | 7 | 100 | 93 |
| 31 | 0.14 | 0.00 | +0.14 | 5 | 85 | 80 |
| 32 | 1.24 | 0.95 | +0.29 | 12 | 110 | 98 |
| 33 | 0.30 | 0.08 | +0.22 | 6 | 90 | 84 |
| 34 | 0.19 | 0.00 | +0.19 | 5 | 90 | 85 |
| 35 | 0.40 | 0.00 | +0.40 | 7 | 95 | 88 |
| 36 | 1.00 | 0.65 | +0.35 | 11 | 110 | 99 |
| 37 | 0.89 | 0.60 | +0.29 | 15 | 105 | 90 |
| 38 | 2.54 | 2.00 | +0.54 | 13 | 100 | 87 |

Fig. 3

## Schematic of oil evaporator

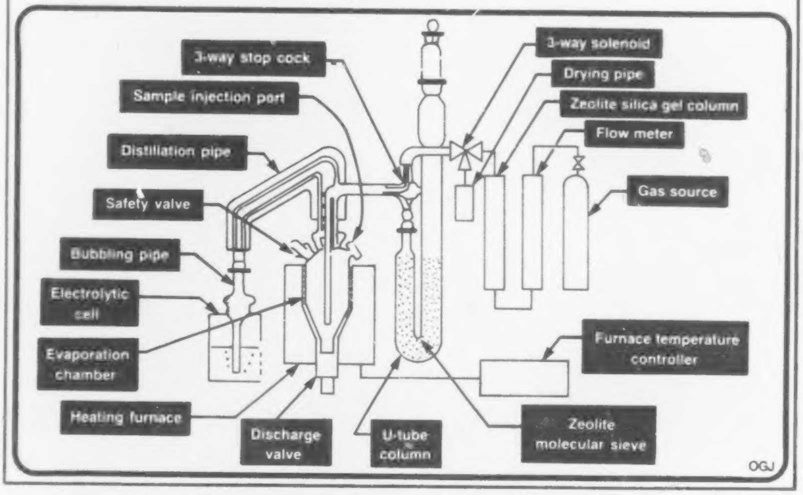


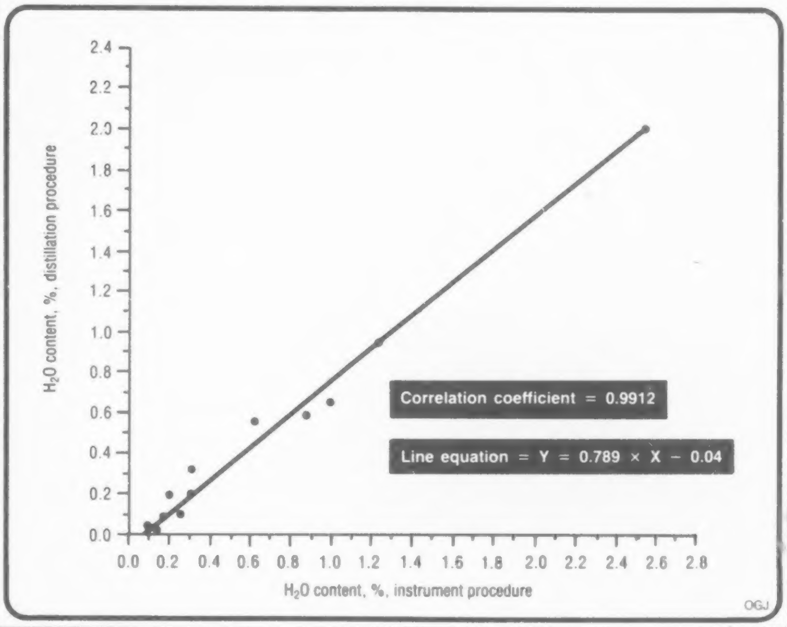
Table 2

## Repeatability of instrumental procedure

| Sample no. | Sample wt., g | $H_2O$ wt., μg | % $H_2O$ | Analysis time, min | Statistics |
|---|---|---|---|---|---|
| 27– 1 | 0.9508 | 1348.6 | 0.1418 | 7 | |
| 2 | 1.1125 | 1469.7 | 0.1321 | 5 | $\bar{x}$ = 0.1328 |
| 3 | 0.8820 | 1178.1 | 0.1336 | 5 | s = 0.0052 |
| 4 | 1.0049 | 1360.6 | 0.1354 | 6 | R = 0.0104 |
| 5 | 1.0377 | 1416.7 | 0.1365 | 6 | |
| 6 | 0.8947 | 1185.6 | 0.1325 | 5 | $\bar{x}$ = mean |
| 7 | 1.0629 | 1404.2 | 0.1321 | 6 | s = standard |
| 8 | 0.9649 | 1301.0 | 0.1348 | 5 | deviation |
| 9 | 0.8959 | 1130.5 | 0.1262 | 6 | R = repeatability |
| 10 | 0.8696 | 1070.5 | 0.1231 | 5 | |
| 30– 1 | 1.2444 | 5240.6 | 0.4211 | 10 | |
| 2 | 0.7994 | 2979.1 | 0.3727 | 5 | |
| 3 | 1.0328 | 4172.8 | 0.4040 | 8 | |
| 4 | 0.8322 | 2723.1 | 0.3272 | 6 | |
| 5 | 1.0101 | 3855.0 | 0.3817 | 7 | $\bar{x}$ = 0.3768 |
| 6 | 0.9468 | 3499.6 | 0.3696 | 7 | s = 0.0261 |
| 7 | 0.9681 | 3429.2 | 0.3542 | 7 | R = 0.0522 |
| 8 | 0.9887 | 3681.9 | 0.3724 | 8 | |
| 9 | 0.8878 | 3288.1 | 0.3704 | 7 | |
| 10 | 0.8510 | 3355.8 | 0.3943 | 7 | |
| 32– 1 | 0.4539 | 5337.4 | 1.1759 | 12 | |
| 2 | 0.4980 | 6591.9 | 1.3237 | 12 | |
| 3 | 0.4048 | 5016.0 | 1.2391 | 10 | |
| 4 | 0.5071 | 6325.9 | 1.2475 | 13 | |
| 5 | 0.4728 | 5987.2 | 1.2663 | 12 | $\bar{x}$ = 1.2295 |
| 6 | 0.3592 | 4237.3 | 1.1797 | 9 | s = 0.0473 |
| 7 | 0.5777 | 7172.6 | 1.2416 | 12 | R = 0.0946 |
| 8 | 0.5167 | 6439.6 | 1.2463 | 11 | |
| 9 | 0.5799 | 6834.5 | 1.1785 | 11 | |
| 10 | 0.6073 | 7265.4 | 1.1963 | 11 | |
| 38– 1 | 0.3136 | 7685.8 | 2.4508 | 17 | |
| 2 | 0.6087 | 15776.2 | 2.5918 | 19 | |
| 3 | 0.3400 | 8800.9 | 2.5885 | 11 | |
| 4 | 0.2863 | 7482.7 | 2.6136 | 10 | |
| 5 | 0.3229 | 8440.4 | 2.6139 | 14 | $\bar{x}$ = 2.5446 |
| 6 | 0.2913 | 7394.4 | 2.5384 | 11 | s = 0.0598 |
| 7 | 0.2382 | 5990.3 | 2.5148 | 11 | R = 0.1196 |
| 8 | 0.3134 | 8058.4 | 2.5713 | 13 | |
| 9 | 0.2545 | 6297.9 | 2.4746 | 11 | |
| 10 | 0.2048 | 5096.8 | 2.4887 | 10 | |

Fig. 4

## Comparison of procedures



the standard distillation procedure which ranged from 0.00% to 2.00% $H_2O$.

This difference (intercept 0.04) may actually be caused by the subjectivity of the distillation procedure to operator influence and limited detection sensitivity of the method. In the ASTM method the operator must handle and transfer the sample and solvent, determine the correct rate of distillation through variations in heat, determine when the distillation is complete, periodically separate the distillate layers physically, and read the results to, at times, less than 0.1 ml of water.

All of these actions are not only sources of error in the system, but actually invite operator bias.

By comparison, the instrumental procedure reduced the number of possible operator errors and bias by eliminating the need to transfer solvent and by performing the titration, endpoint detection, and concentration calculations automatically with a hard copy printout of results.

The only operator-dependent duties include the weighing and injection of sample and introduction of fresh solvent from a reservoir to an etched level marking on the chamber by means of a stopcock.

In this way, more-consistent results are obtained even when the procedure is performed by many different operators. This allows enhanced flexibility in laboratory operation.

**Precision.** Table 2 shows the repeatability of the instrumental procedure for 10 consecutive runs of the same sample for four separate samples of various moisture contents, along with the statistical summary for each.

Column 1 is the sample weight in grams, for each determination. Attempts were made to ensure the consistency of sample weight for each particular series of determinations. However, due to the variability of sample injection, the weights modulate to some extent.

Column 2 represents the weight of water, in micrograms, detected by the electrolytic titration. Column 3 is the percent water printed at the end of each run, and Column 4 is the analysis time in minutes.

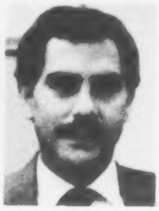
Column 5 shows the results of the statistical evaluations performed for each group of determinations. These are the mean (X), standard deviation (S), and repeatability (R) calculated as R = S × 2.

The repeatability of the instrumental procedure ranged from 0.01% to 0.12% as the mean result for water content ranged from 0.13% to 2.54%. The study demonstrated a >100% improvement in repeatability over a broader range with the instrumental procedure as compared to the established repeatability of the standard ASTM procedure.

When the results in Table 2 are

## The authors. . .

**Kunkel**



**DeSandro**

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averaged, the instrumental procedure exhibits a repeatability of 0.07% for a range of 0.0-2.5% $H_2O$, where the ASTM procedure defines its repeatability, with sample volumes of 50 ml, as 0.20% for the range 0.0-2.0% $H_2O$. The repeatability for the distillation method was not performed since it has been done previously and is prescribed in ASTM D95-83.

The true repeatability of the instrumental procedure may not have been realized in the study. A repeatability nearer the actual system value of 0.05% (the value obtained from 20 determinations using 1 ml sample size of 1 mg/ml water-methanol standard) may be realized if the sample weights could be held at a constant value within a group of determinations.

This would be a prime area for further study, as would an investigation of the reproducibility between results from different laboratories for the same sample, using different operators and equipment.

**Detection sensitivity.** The detection sensitivity of the standard distillation procedure is very limited, with the lowest measured result of 0.04% $H_2O$ in sample No. 19. It can be seen in Table 1 that 24 out of 38 sample determinations were 0.00% $H_2O$ with the ASTM method, which indicates either no water detected or trace amounts (less than 0.05 ml $H_2O$) collected) that could not be given reliabie volumes and were given values of 0.00% $H_2O$.

Results for the same samples using the instrumental procedure ranged from 0.01% to 0.40% $H_2O$. The lowest measured value for this method was 0.01% because the results were rounded to two decimal places for ease of comparison. However, the actual detection limit of the instrumental procedure is 10 μg of $H_2O$. If a 10 gram size is used the lowest measured value could be 0.0001% $H_2O$.

**Analysis time.** A major advantage of the instrumental system is reduced analysis time. As can be seen in Table 1, the average analysis time recorded for the 38 samples measured was 5.7 min for the instrumental procedure and 87.9 min for the standard distillation procedure.

This implies that 15 samples could be analyzed by the instrumental-system in the same time it takes to analyze one sample by the ASTM procedure. This ratio can be countered by utilizing several distillation assemblies at one time, although this approach would increase equipment costs and decrease laboratory space.

Small analysis sample volume is another feature of the instrumental procedure. When working with heterogeneous materials, it is generally believed that the larger the analysis sample, the more representative the results.

This would indicate that the instrumental results are less representative of the entire sample than are those of the distillation method. However, due to the reduced analysis time of the instrumental system, a sample can be analyzed in duplicate or even in triplicate to verify analysis representation, and still be completed in less time than it takes to perform a single distillation.

Although the currently accepted standard distillation method is considered reliable and well proven, the instrumental moisture determination system was shown to be comparable in accuracy and superior in precision and detection sensitivity with reduced analysis time. The instrumental procedure is also reagent efficient, less vulnerable to operator bias, and is easily operated.

Based on the results of the study, the instrumental moisture determination system is a valid and recommended alternative for measuring water content in' petroleum products and bituminous materials.

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## TECHNOLOGY

# Diesel cloud point determination needs uniformity

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Cloud point values for diesel fuels, measured by the existing ASTM method, can vary by as much as 8° C. depending on the apparatus and technique used. These variations have an important effect on diesel-blending formulations.

Research conducted at NOVA/Husky reveals cloud point discrepancies in results obtained by different laboratories testing the same fuel, and the impact of the discrepancies on blend ratios of distillates which, in turn, affect refinery economics.

The major causes for the discrepancies, and recommended changes in test equipment specifications and test procedures to test the discrepancies, are presented in this article.

**Cloud point test.** Cloud point determination is a standard ASTM test (D2500) that has been used by the petroleum refining industry for a long time to monitor the quality of diesel under low temperature. This test gives an indication of the temperature at which crystallization of paraffins begins in the fuel.

Because the presence of wax crystals formed naturally would impede the flow of diesel through fuel filters of vehicles, it is imperative that the diesel quality be adjusted such that the cloud point temperature stays below the normal operating temperature of vehicles.

This adjustment is performed during diesel blending. In the refinery, diesel is produced by blending distillate fractions in the boiling range of 150° C. to 350° C. Within this range, typically three distillate fractions are available; they are commonly referred to as light, intermediate, and heavy distillates.

To obtain low cloud point diesel, the relative amount of light to the heavier (intermediate and heavy) distillates has to be increased. In most parts of Canada and the northern regions of the U.S., the amount of heavy distillate that can be blended into winter diesel grades is small. Light distillate is the major component of these diesels.

The blending requirements, in many instances, do not match the yield distribution of the refinery, even in situations where catalytic cracking units are available.

Consequently, it is not uncommon to have a situation in which there is a shortage of light distillate, and at the same time, a surplus of heavy distillate during the winter season. The shortage of light distillate may impose a constraint on diesel production rate, whereas the surplus of heavy distillate may create storage and marketing problems.

To deal with this imbalance problem, there are several alternatives available for consideration, which may include bringing in light distillate from another refinery, conversion of heavy distillate into lighter products, and using chemical additives to improve flow properties.

Implementing any of the above may be quite costly. Before a solution is sought, it is important to examine the cloud point test closely because, in many instances, the test is the criterion for qualify-

Table 1

## Results of Canadian General Standards Board study

| | Fuel | | | | |
|---|---|---|---|---|---|
| **Company** | **C** | **D** | **E** | **F** | **G** |
| | | | Cloud point, °C. | | |
| 1 | −14 | −26 | −25 | −17 | −14 |
| 2 | −14 | −25 | −22 | −14 | −15 |
| 3 | −15 | −25 | −21 | −16 | −15 |
| 4 | −15 | −25 | −21 | −14 | −14 |
| 5 | −16 | −24 | −21 | −14 | −15 |
| 6 | −17 | −26 | −20 | −13 | −14 |
| 7 | −15 | −25 | −21 | −14 | −15 |
| 8 | −14 | −26 | −25 | −17 | −14 |
| 9 | −18 | −25 | −23 | −19 | −16 |
| Mean. | −15 | −25 | −22 | −15 | −15 |
| Max. | −14 | −24 | −20 | −13 | −14 |
| Min. | −18 | −26 | −25 | −19 | −16 |
| St. dev. | 1.4 | 0.9 | 1.9 | 2.0 | 0.7 |

ing the extent of the problem, as well as gauging the degree of success of a proposed solution.

**Cloud point variations.** In a round robin study conducted by the Canadian General Standard Board (CGSB) in 1985, nine refinery and research laboratories participated in the testing of five diesel fuels. Results are shown in Table 1. The discrepancy between laboratories ranged from 2° C. for Blends D and G, to 6° C. for Blend F.

In another study, conducted through the Canadian Cooperative Fuel Exchange Program (under the auspices of CGSB) on diesel cloud point, a winter-grade diesel was tested by approximately 30 refinery and research laboratories in Canada. Results are shown in Table 2.

The discrepancy between laboratories was large; a maximum discrepancy of 20° C. was observed. However, a plot of the number of the response vs. cloud point (Fig. 1) indicates that most laboratories (85% of total response) reported results within an 8° C. range centered on the mean.

In other studies that NOVA/Husky Research has been involved in, a discrepancy of 6° C. between different sets of equipment (manufactured by different companies) was found, even when the tests were performed by the same operator under well-controlled conditions. All the equipment used was, according to the manufacturers, fabricated in conformity with ASTM specifications.

**Blend effects.** The discrepancy in cloud point measurements of the magnitude mentioned above could have a strong impact on the blend ratio required to achieve a certain cloud point target. In meeting the cloud point specification of a certain geographical region, refineries using different cloud point equipment may be producing diesel fuels with quite different low-temperature properties.

For illustration purposes, the impact on two winter-grade (I and II) diesels are discussed. The desired cloud points for Grades I and II are −23° C. and −32° C., respectively.

Three distillate streams with typical characteristics (Table 3) were used as blending components. Two sets of equipment (A and B), made by different manufacturers, were used in this study.

The cloud point determined by Equipment A was approximately 6° C. higher than those measured by Equipment B. The causes of discrepancy will be discussed later.

The blending formulas for Grades I and II were developed separately using Equipment A and B. The objective was to maximize the use of heavy and intermediate distillates. The results are shown in Table 4.

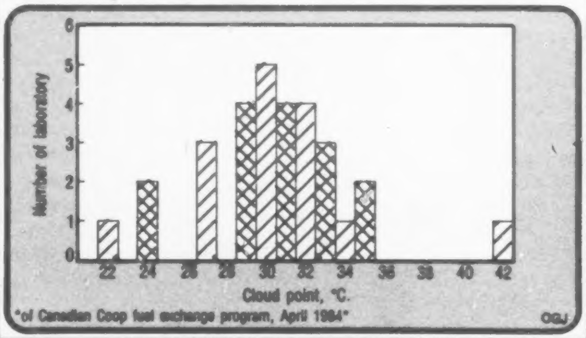
For diesel Grade I, only 5% heavy distillate could be used in the blend according to Equipment B. For diesel Grade II, only light and intermediate distillates were used in the blend, and the objective was to maximize the use of intermediate distillate. According to Equipment A, 25% of intermediate distillate could be used, whereas Equipment B indicated that 40% could be used.

For a refinery that experiences a shortage of light distillate, and a surplus of heavier distillates in winter, it is clearly advantageous to use Equipment B, which allows higher concentrations of heavier distillates in winter diesel blends. For the purpose of producing diesel with uniform cloud point characteristics, only one type of equipment should be used. In that case, one may ask, "What equipment should be used?" and "Why does the equipment made by different manufacturers give different cloud point results?"

**Discrepancy causes.** Numerous factors could account for the variations in cloud point measurement. Some of these factors may involve human error and equipment failure. Since these particular factors do not occur consistently, and their impact varies depending on individual circumstances, they are not the subject of the discussion that follows. The focus is on factors that occur frequently and the

Fig. 1

Cloud point distribution*

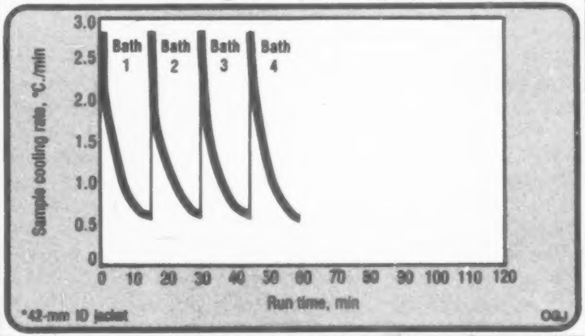


*of Canadian Coop fuel exchange program, April 1984*

OGJ

Fig. 2

Rate of cooling plays important role*



*42-mm ID jacket

OGJ

Table 2

## Canadian Cooperative Fuel Exchange test results*

| Company | Cloud point, °C., (ASTM D-2500) Result | Deviation |
|---|---|---|
| 1 | −30 | 0 |
| 2 | −35 | −5 |
| 3 | −34 | −4 |
| 4 | −29 | +1 |
| 5 | −33 | −3 |
| 6 | −32 | −2 |
| 7 | −42 | −12 |
| 8 | −30 | 0 |
| 10 | −29 | +1 |
| 11 | −27 | +3 |
| 12 | −29 | +1 |
| 13 | −32 | −2 |
| 14 | −31 | −1 |
| 15 | −30 | 0 |
| 16 | −31 | −1 |
| 17 | −24 | +6 |
| 18 | −31 | −1 |
| 19 | −30 | 0 |
| 20 | −33 | −3 |
| 21 | −29 | +1 |
| 22 | −32 | −2 |
| 23 | −27 | +3 |
| 24 | −35 | −5 |
| 25 | −32 | −2 |
| 26 | −27 | +3 |
| 27 | −24 | +6 |
| 28 | −33 | −3 |
| 29 | −22 | +8 |
| 30 | −30 | 0 |
| Average | −30.5 | ±2.7 |
| Maximum | −22 | 8 |
| Minimum | −42 | 11 |
| St. Dev. | | 3.9 |
| Max. Dev. | | 12.1 |

Sample No. D-97, April 1984.

Table 3

## Typical characteristics of light, intermediate, and heavy distillates

| | Light | Intermediate | Heavy |
|---|---|---|---|
| Gravity, °API | 44 | 38 | 35 |
| **Distillation, °C** | | | |
| IBP | 155 | 227 | 232 |
| 10% | 170 | 255 | 260 |
| 50% | 200 | 282 | 300 |
| 90% | 230 | 293 | 332 |
| EP | 245 | 310 | 360 |
| **Paraffin carbon Number distribution** | $C_9$ to $C_{10}$ | $C_{11}$ to $C_{20}$ | $C_{11}$ to $C_{25}$ |

Table 4

## Comparison of blend formulas using Equipment A and B*

| Winter Diesel Grade | Cloud point target, °C. | – Blend formula – vol % Equipment A L-I-H† | Equipment B L-I-H† |
|---|---|---|---|
| I | −23 | 75-20-5 | 71-19-10 |
| II | −32 | 75-25-0 | 60-40-0 |

*For winter diesel grades I and II.
†L-I-H denotes light-intermediate-heavy distillate blend formulation in volume percent.

impact that can be quantified.

Under the conditions where the operator is experienced and the ASTM procedures are carefully followed, it is not uncommon to observe cloud point variations of 8° C. between different equipment. The factors that were commonly found to be responsible, and their influence, are listed in Table 5.

Among the factors listed, the rate of cooling plays the most important role. Following the ASTM method, the rate of cooling experienced by diesel is not constant through the run, but is cyclical in nature.

The cooling rate of a winter diesel as a function of run time is shown in Fig. 2. The number of cycles is determined by the number of baths used, where one cycle corresponds to one bath.

The range of the cooling rate within each cycle is mainly determined by the dimensions of several crucial parts of the apparatus (Fig. 3), particularly those that determine the thickness of the air gap between the test jar and the jacket.

Because ASTM D2500 allows a range of jacket diameter (ID between 42 and 50 mm) that can be used, the range of cooling rate is different for different internal diameters. As will be apparent later, the difference in cooling rate between a 42-mm ID jacket and a 50-mm jacket is large, and could account for a cloud point variation of approximately 4° C.

The air temperature in the gap between the test jar and jacket is also important because it affects the rate of heat transfer from the diesel sample to the cooling medium. According to the ASTM method, the top part of this gap is open, and thus free exchange of warmer room air with the air inside the gap is possible.

However, some equipment manufacturers provide their customers with gaskets made of felt or other material to seal off the top part of the air gap to reduce frost formation. As a result, the air temperature in the gap is lowered and the cooling rate increased.

Many manufacturers also provide stoppers to cover the top part of the jacket when the test jar is not in place. This feature has an effect similar to that of the felt gasket. The use of the top gasket and the stopper should increase the cloud point by approximately 2° C.

The authors have conducted a large number of experiments with jackets of different internal diameters within the range specified by ASTM. The use of a top gasket and stopper was also a variable.

In all of these experiments, winter diesel Grade I was used. The cloud point temperature and the cooling rate at the cloud point were recorded. Results are summarized in Fig. 4, which is a plot of cloud point vs. cooling rate.

It is obvious that at cooling rates above 0.7° C./min, cloud point increases with increasing cooling rate. Within the range of cooling rates studied, cloud points varied from −23° C. to −29° C. At cooling rates less than 0.7° C./min, the cloud point was not affected by the cooling rate.

To provide more detailed information, Fig. 2 presents the cooling rate of winter diesel in an apparatus that uses 42-mm ID jackets and a felt gasket and stopper. Cooling was very rapid (2.8° C./min) at the beginning of each cycle, then declined to 0.6°C./min in approximately 15 min.

Cloudiness was observed almost immediately after the sample was transferred into the fourth bath. At that moment, the cooling rate was around 2.8° C./min and the cloud point temperature was −23° C. Within each 15-min cycle, there were 10 min in which cloud point was sensitive to cooling rate, and only 5 min in which cooling was slow enough that cloud point was not affected. The entire analysis took approximately 60 min.

Several experiments were performed with the 42-mm ID jacket, but without the stopper and felt gasket. A typical coolng rate vs. run time plot is shown in Fig. 5.

The peak cooling rate was reduced from 2.8° C./min to 2.6° C./min. The cycle time was extended to 20 min from 15 min. In each cycle, there were 10 min (instead of 5 min) in which the cooling rate was lower than 0.7° C./min.

The cloud point of winter diesel was recorded at −26° C., and the cooling rate at that moment was 1.5° C./min. The entire analysis took approximately 70 min.

In experiments where a large diameter jacket (50 mm) was used with a felt washer and stopper, the cooling rate (Fig. 6) dropped from a peak value of 1.6° C./min to 0.4° C./min in 30 min. Within each cycle, there were 22 min in which the cooling rate was lower than 0.7° C./min. The cloud point of winter diesel was recorded at −29° C.

These experiments showed that larger diameter jackets had longer time durations in which the cloud point was not affected by the cooling rate. The disadvantage of using a large diameter was the longer time (120 min for a 50-mm jacket vs. 60 min for a 42-mm jacket) required to complete one analysis.

The above experiments showed that small changes in equipment set up could change the cloud point of the same fuel by 6° C. Because the cooling rates of the ASTM equipment are cyclical, fuels with natural cloud points slightly higher than the transfer temperature are less susceptible to variation. Because the cooling rates of the ASTM equipment are cyclical, fuels with natural cloud points slightly higher than the transfer temperature are less susceptible to variation, because the cooling rate prior to tube transfer is typically low.

The fuels that are most susceptible to cloud point variation are those with cloud points several degrees lower than the transfer temperature. This type of fuel is subjected to a high cooling rate at about the moment cloudiness is formed.

Table 5

## Common factors responsible for cloud point variation

| Factors | Approximate cloud point variation |
|---|---|
| Cooling rate of equipment | 6° C. |
| Operator's judgment | 1° C. |
| Thermometer calibration | 1° C. |
| Cumulative result | 8° C. |

The study also found that cloud point variation caused by different operators is approximately 1° C., assuming the operators are experienced and the tests are performed carefully according to ASTM procedures. It is also common to find thermometers used in cloud point tests that are off calibration by 1° C.

**Possible improvements.** It is possible to reduce the discrepancy between the laboratories by adopting one of the following two approaches. The first approach involves tighter specification of the equipment parts to ensure that the cooling rate cycles are close to identical for all equipment. The other approach involves removing the cooling rate cycle altogether and replacing it with a constant rate of cooling during measurement.

For the first approach, the following actions are recommended.

1. Specify the thickness of the air gap between the sample vial and cooling jacket. To do so, the existing specification for internal diameters of sample and cooling jackets would have to be tightened by replacing the range of diameters with more exact values. To avoid excessive sensitivity to cooling rates, an air gap of about 13 mm would be suitable.

2. According to the existing method, the jacket can be made of metal or glass, both of which have very different thermal conductivities. In addition, the thickness of the material is currently not specified in the method. Because both the material and the thickness would affect the cooling rate, it is important to specify both.

3. There should be an agreement on whether or not a tight felt gasket should be used between the sample vial and jacket. The use of this gasket would increase the cooling rate and cause more variability in results. The advantage in using the gasket is the reduction of frost formation and, hence, less work is required to maintin the jacket in a dry condition.

With the specification approach, the changes to the existing equipment are relatively minor because the cooling baths can still be used. The discrepancy caused by equipment differences should be reduced. However, the cooling rate is still cyclical and the technique is not a consistent indication of fuel properties because different fuel blends may experience different cooling rates at the instant of cloud formation.

The second approach involves the elimination of cooling rate cycles. The cooling rate is maintained at a constant level which is low enough to minimize its influence on the cloud point.

Based on our study, a cooling rate

Fig. 3

Typical cloud point apparatus

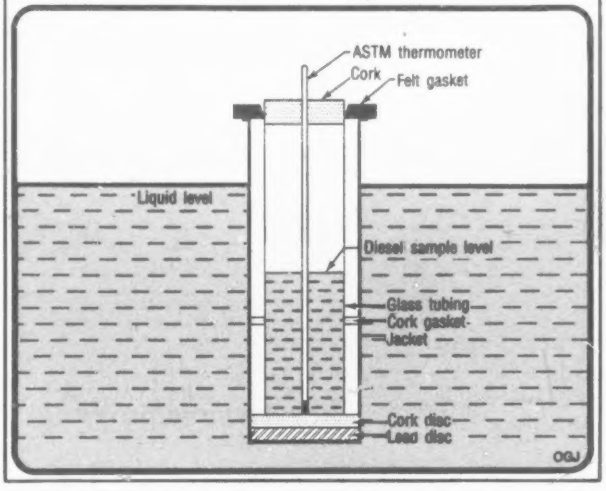
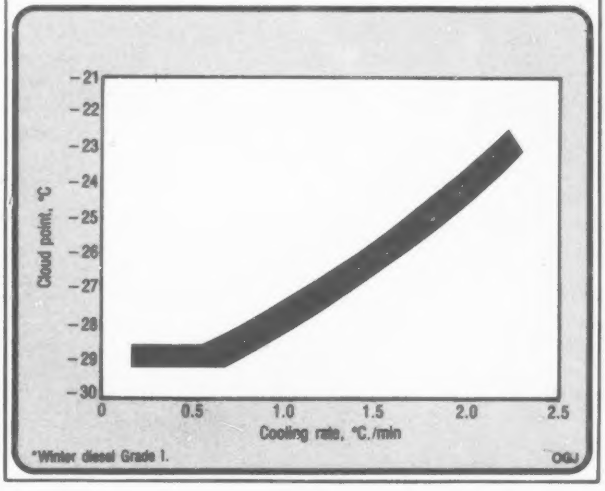


Fig. 4

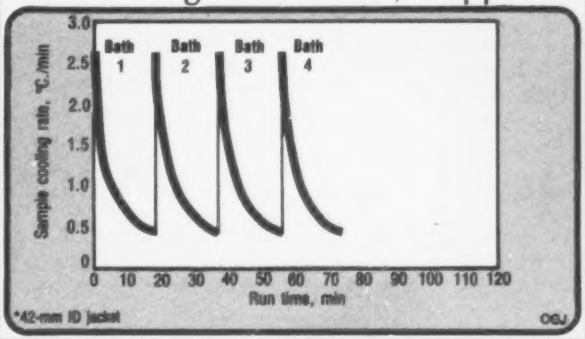
Cloud point rises with cooling rate



*Winter diesel Grade I.

Fig. 5

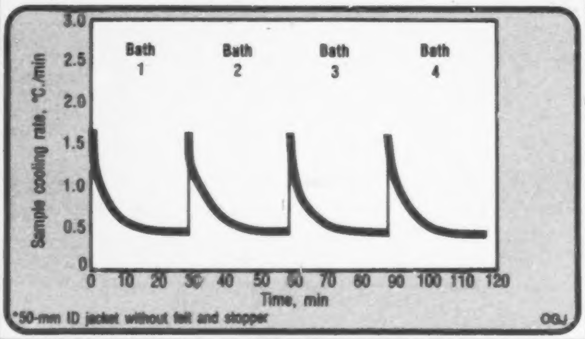
## Peak cooling without felt, stopper*



*42-mm ID jacket

Fig. 6

## Larger diameter jacket drops cooling*



*50-mm ID jacket without felt and stopper

in the range of 0.5 to 0.8° C./min seems appropriate. Only one cooling bath is needed, but the bath temperature has to be programmed such that it decreases with time.

Compared with the first approach, this approach requires more extensive changes to the existing equipment and consequently, higher costs for the modifications. But the advantage is better consistency, and the cloud point is reproducible. Because the cloud point has a significant effect on fuel performance and refinery economics, both approaches deserve serious consideration.

### Acknowledgment

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# Fresh FCC catalyst tests predict performance

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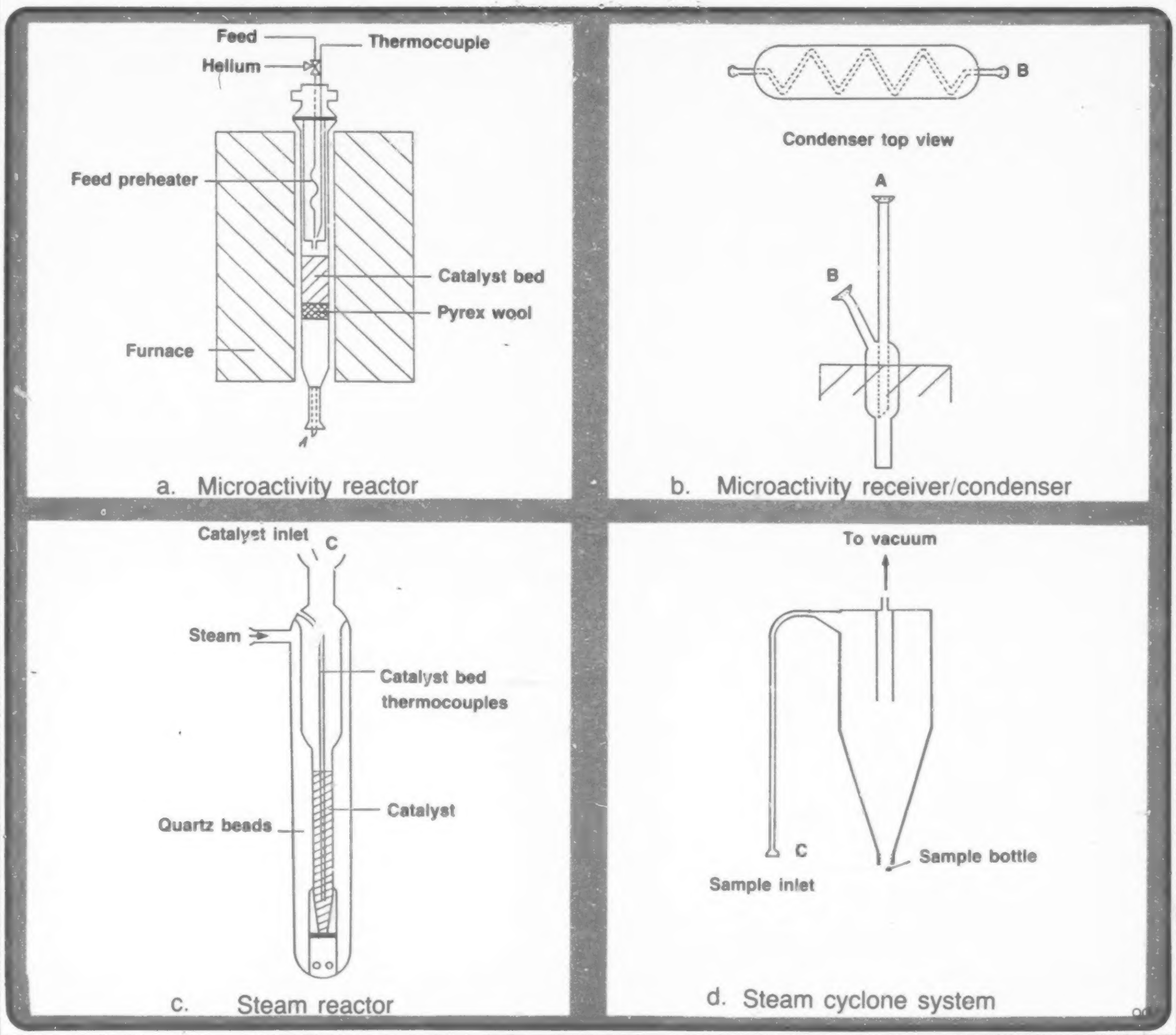
There are dozens of fluid catalytic cracking (FCC) catalysts available to refiners, and choosing the best one for any application can be a challenging task. The choice is critical because using the wrong FCC catalyst can cost a refiner millions of dollars per year in product value.[1]

Thus, when confronted with several catalyst proposals from different suppliers, the refiner needs accurate information about the performance of each catalyst. In almost all cases, yield differences between catalysts are far more important to the refiner's bottom-line profits than are catalyst costs. Unfortunately, yield differences are difficult to identify due to the dynamic nature of commercial FCC operations.

How can the refiner develop accurate catalyst performance comparisons? Which tests most accurately correlate with commercial performance? Is there a good method of

Fig. 1

Microactivity and steam deactivation test apparatus


Feed
Helium
Thermocouple
Feed preheater
Catalyst bed
Pyrex wool
Furnace
B
Condenser top view
A
B
Catalyst inlet
C
Steam
Catalyst bed thermocouples
Catalyst
Quartz beads
To vacuum
C
Sample inlet
Sample bottle

a. Microactivity reactor

b. Microactivity receiver/condenser

c. Steam reactor

d. Steam cyclone system

Fig. 2

## Microactivity tests on fresh catalyst

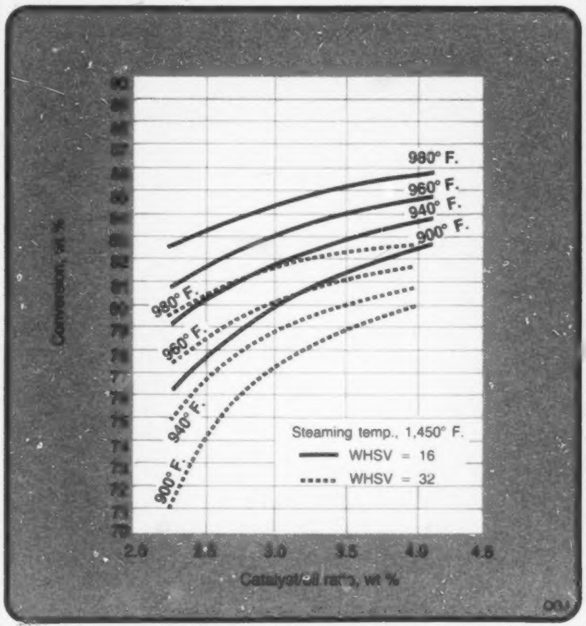
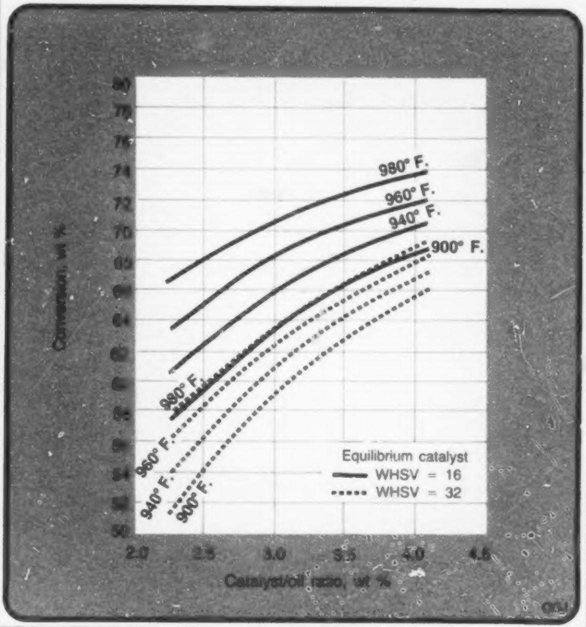


Fig. 3

## Tests on equilibrium catalyst



evaluating resid cracking catalysts? These are just a few of the questions this article will address.

Since the topic of catalyst evaluation is so broad, the focus will be on only one aspect of catalyst evaluation: testing fresh FCC catalysts for the purpose of predicting commercial performance. Future articles will examine testing of equilibrium catalysts and evaluation of actual commercial catalyst performance via commercial test runs.

Steam deactivation and microactivity testing (MAT) equipment will first be described. This is followed by a summary of an effective and realistic approach for evaluation of fresh FCC catalysts. Finally, the questions of steaming severities and MAT conditions are addressed.

As is the case with most complex subjects, there are few absolute right or wrong methods in catalyst evaluation. The intent here is to discuss various catalyst evaluation techniques and present some guidelines as to test conditions that have been used successfully to simulate commercial catalyst performance.

**Equipment and techniques.** Precise control of microactivity and steam deactivation conditions is of para-

Fig. 4

## Typical commercial iso/olefin ratios

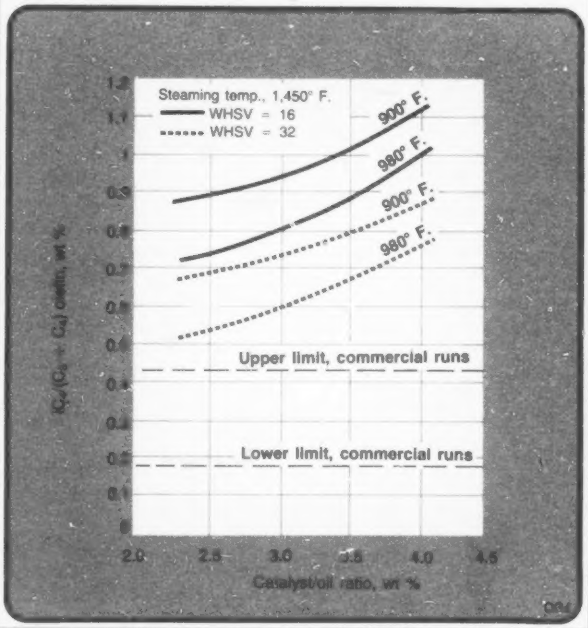


Fig. 5

## MAT conditions on iso/olefin ratio

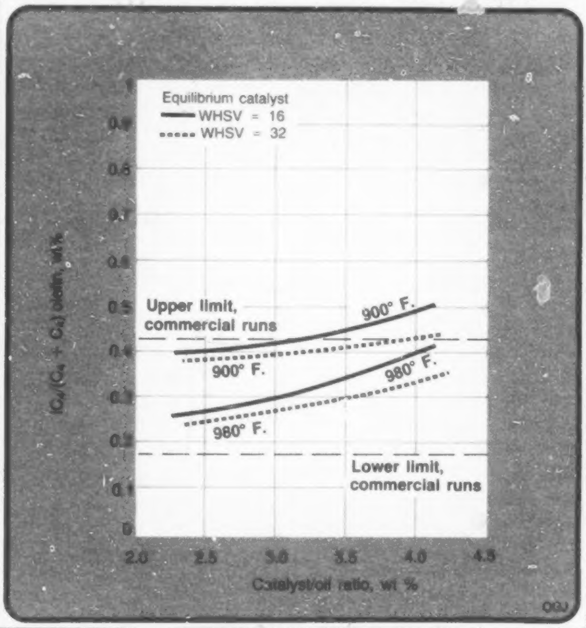


Fig. 6

Temperature based steam deactivation

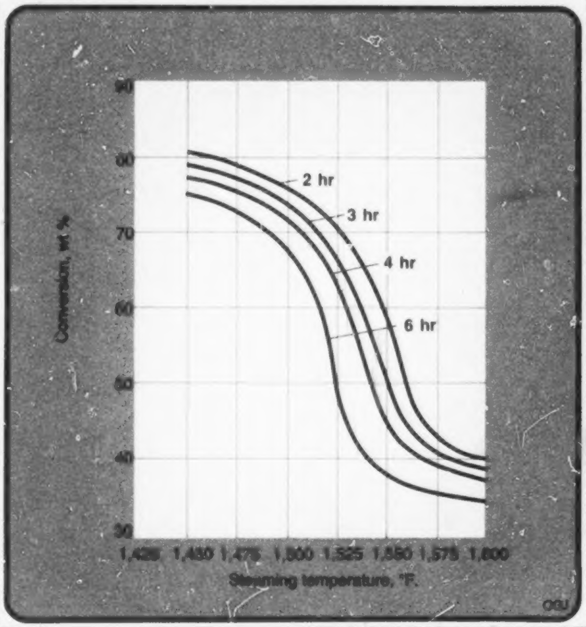
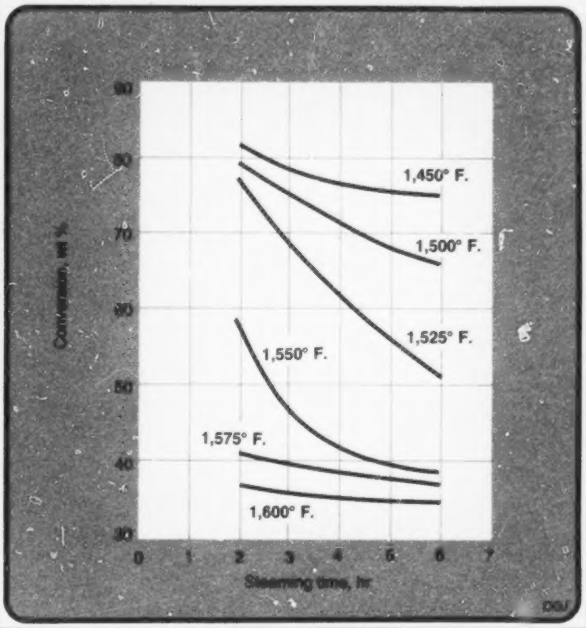


Fig. 7

Time based steam deactivation



mount importance. The apparatus must be of the highest caliber to obtain accurate results. Fig. 1 shows the equipment used for this study.

The microactivity unit reactor (Fig. 1a) is constructed from quartz. Quartz offers the advantage of being able to visually verify cleanliness necessary for accurate weight balances.

The product collection system specified in ASTM method D-3907 is not sufficient for use at higher reaction temperatures.[2] A receiver and condenser system which assures 99 wt % recoveries at temperatures up to 980° F. is shown in Fig. 1b.

During the run, the liquid receiver is inserted into an acetone/dry ice bath. The receiver is then immersed in an ice water bath immediately after the feed injection is complete. This procedure ensures efficient separation of components and consistently high weight balances. The reactor feed tube insert (deadman) is described as follows:

- The internal tubing length is 10 in., with three minor kinks to prevent rapid expansion of vapor with consequent expulsion of a possible liquid oil plug.
- The ASTM coil outside the body of the reactor is eliminated to prevent thermal cracking and plugging with heavy feeds.
- Purge gas should be helium, not nitrogen. This is indicated by the data in Table 1, which show the results of studies conducted on the effects of He, $N_2$, and air as the purge gas both at preheat and run stages. The outstanding feature to note is that the hydrogen yields with the $N_2/N_2$ gases are twice that with the He/He gases.

The reactor for the steam deactivation unit consists of two concentric quartz (Si, 96 + %) tubes (Fig. 1c). The sample volume is 30 ml to allow for duplicate MAT runs. The inner tube is surrounded by live steam, which maintains the fluidized catalyst bed at ± 2° F. (limited by thermocouple sensitivity).

The sample is withdrawn from the steamer by use of a cyclone under slight vacuum (Fig. 1d). Deionized water is pumped into a 650° F. preheat zone, and is heat traced to the reactor. Nitrogen is controlled by a mass flow controller, and is preheated and thoroughly mixed with the steam. The nitrogen feed rate is 5 cc/min, while the liquid water rate is controlled at 10 cc/hr.

**Physical and chemical tests.** The first step in evaluating catalysts is to examine physical and chemical properties. One can learn a great deal about how a catalyst should perform from relatively simple analyses. A list of some key analyses and required instrumentation is presented in Table 2.

The alumina content of current commercial FCC catalysts can be measured by using various elemental analysis techniques, including inductivity coupled plasma atomic emission spectroscopy (ICP-AES); atomic absorption spectroscopy (AAS); and X-ray fluorescence (XRF) spectroscopy. Of course, measuring the bulk alumina content by these methods will not differentiate between amorphous and crystalline alumina.

This distinction can be made, however, using X-ray diffraction (XRD). The crystalline alumina content affects matrix activity and, in turn, the catalyst's ability to crack heavy gas oil and resids. Crystalline alumina and other proprietary matrix additives are also effective in protecting the zeolite from nitrogen and vanadium poisoning and in reducing $SO_x$ emissions.[3, 4]

Defining zeolite type is helpful in evaluating how a catalyst will perform. As the silica/alumina ratio of the zeolite increases, the unit cell shrinks. A typical Y zeolite has a unit cell of about 24.68 Å compared to about 24.55 Å for an ultra-stable Y (USY) zeolite. Generally, USY zeolites will have less initial activity, better stability, lower coke selectivity, and will produce higher-octane gasoline than conventional Y zeolites.[5]

Unit cell size, however, is not the only criteria that should be considered in examining ultrastable zeolites. As these zeolites are transformed from Y to USY, aluminum is removed from the framework. If proper steps are not taken (i.e., acid leaching), this non-framework aluminum will remain in the zeolite and block the access of the feed molecules into the zeolite cages, thus reducing the zeolites' effective activity and catalyzing gas make.

Consequently, it is important to determine whether or not the aluminum has been pulled out of the zeolite altogether or only out of the frame-

Table 1

## Comparison of preheat/run gases microactivity*

| Preheat/run | Low metal catalyst (520 ppm Ni + V), wt % Conv. | Coke | $(C_1\text{-}C_4)$ | $H_2$ | High metal catalyst (8,490 ppm Ni + V), wt % Conv. | Coke | $(C_1\text{-}C_4)$ | $H_2$ |
|---|---|---|---|---|---|---|---|---|
| Air/He | 68 | 2.2 | 11.7 | 0.031 | 47 | 3.6 | 6.0 | 0.941 |
| He/He | 67 | 2.4 | 11.5 | 0.015 | 46 | 3.5 | 5.7 | 1.065 |
| $N_2/N_2$ | 66 | 2.4 | 10.2 | 0.035 | 46 | 3.7 | 5.6 | 2.349 |

* ASTM MAT conditions.

Table 2

## Key analyses and instrumentation

| Analysis | Instrument |
|---|---|
| Crystalline $Al_2O_3$ | XRD |
| Zeolite content | XRD, Benesi |
| Zeolite type (unit cell) | XRD, IR |
| Framework/non-framework aluminum | $^{27}$Al NMR, IR* |
| La/Ce ratio | Chemical (ICP, AA, XRF) |
| Surface area | Commercial apparatus |
| Pore size distribution | Commercial apparatus |

* Infrared

work. The unit cell will shrink in either case, and the infrared spectra will change. $^{27}$Al (isotope) magic angle spinning nuclear magnetic resonance (NMR) spectroscopy can be used to pick out the presence of nonframework aluminum.[6, 7]

The ratios of rare earth components in the zeolite are also important. Most significant is the ratio of La/Ce. For a given rare earth content, a higher La/Ce ratio will result in a significantly more stable zeolite.

Surface area and pore size distribution also provide valuable information on expected catalyst performance. A catalyst which has a high percentage of small pores is susceptible to diffusion limitations with heavy oils and to pore mouth plugging at relatively low levels of residual carbon. The combination of small pores and high surface area leads to stripping problems and hydrocarbon carry over to the regenerator.

In addition to the inspections listed in Table 2, there are a host of other analyses which can be related to catalyst performance. These include sodium, iron, titanium, pore volume, attrition index, density, and particle size distribution just to name a few. The significance of these analyses is generally known and will not be discussed here.

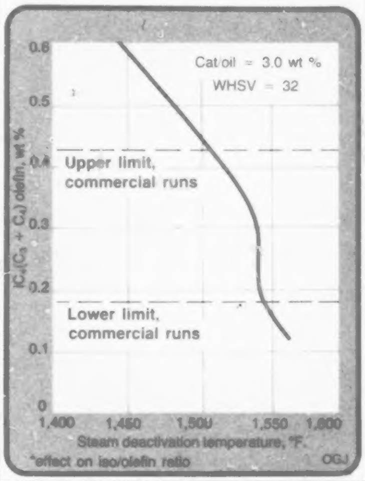
**MAT testing.** One of the most useful tools for evaluating fresh catalysts is the microactivity test. Several MAT runs are required to adequately characterize a catalyst's potential.

The first tests are done after steaming at different severities using a standard vacuum gas oil (VGO). MAT results after mild steam deactivation give a good indication of the inherent activity and selectivity.

MAT evaluations after severe steam deactivations are obtained to determine relative catalyst stabilities and to simulate what the yield selectivities would be after encountering severe commercial regeneration conditions. The optimum MAT conditions and the definitions of "mild" and "severe" steam deactivations remain key questions in the industry and have been the subject of some controversy.

Fig. 8

## Deactivation temp.*



*effect on iso/olefin ratio

A 2-hr procedure with approximately 95% steam (balance $N_2$) at temperatures between 1,450° F. and 1,550° F. has been used successfully at Filtrol. MAT conditions are: 3.0 cat/oil ratio, 37.5 sec., 32 weight hourly space velocity (WHSV), and 960° F.

Another MAT evaluation is done after impregnation of metals. The catalyst is impregnated with appropriate levels of metals (typically 3,000 ppm each of Ni and V) using nickel and vanadium naphthenates.[8]

The metals are then equilibrated via a low temperature (1,350° F.), 10-hr steaming before the catalyst is steam deactivated at 1,450° F. for 2 hr. The metals-loaded catalyst is evaluated with a resid containing feedstock.

Results from this type of test correlate much more accurately with a catalyst's resid cracking ability than do results from tests with lighter feedstocks. Table 3 presents inspections of the standard gas oil and the resid containing feeds used in research MAT tests.

Table 4 presents examples of results from the tests described. Four current commercial FCC catalysts are compared. Catalyst "A" has an amorphous alumina-based matrix. Catalyst "B" is silica based. Catalyst "C" is clay based, and catalyst "D" contains significant amounts of crystalline pseudo-boehmite alumina in the matrix.

The catalysts with the low activity matrix materials (silica and amorphous alumina) show the poorest light cycle oil/decanted oil ratios, coke selectivities, stabilities, metals tolerance, and resid cracking abilities (Table 4).

These differences can be explained by the fact that the large, heavy molecules cannot completely enter the zeolite cage and must be precracked by the matrix. An inactive matrix will simply provide these molecules with a site to absorb and thermally degrade to coke.

The differences observed between the catalysts with the resid feed after metals impregnation are much larger than those observed after mild steam deactivation. These results show that *differences between catalysts are strongly dependent on exactly how the catalysts are tested.*

Consequently, it is imperative that the feedstocks and conditions used for the tests are those that most closely correlate with the commercial operation. No steam deactivation procedure or MAT test can correlate perfectly with commercial performance. However, if reliable commercial data or pilot plant data are not available, the above procedures can give an excellent indication of relative catalyst performance for a wide variety of commercial applications.

**Optimizing test conditions.** Because the method of catalyst evaluation can profoundly affect the results, a study was conducted to identify the most realistic overall MAT and steam deactivation conditions. Two commercially available catalysts were used in this study, one fresh and one equilibrium. The study involved varying reactor temperatures, cat/oil ratios, space velocities, and steam deactivation conditions.

Figs. 2 and 3 illustrate the effects of catalyst/oil ratios and space velocities on conversions. The slope of the con-

Table 3

## Charge stock inspections

| Feed | Standard gas oil | Resid* blend |
|---|---|---|
| **FCC charge quality** | | |
| Gravity, °API | 28.40 | 25.00 |
| Sulfur, wt % | 0.63 | 0.70 |
| Nitrogen, wt % | 0.11 | 0.18 |
| Carbon residue, wt % | 0.33 | 2.66 |
| Aniline pt., °F. | 190.00 | — |
| Nickel, ppm | 0.10 | 4.10 |
| Vanadium, ppm | 0.20 | 1.60 |
| **Vacuum distillation, D1160, °F.** | | |
| 10% at 760 mm | 584 | 598 |
| 90% | 999 | 1019 (80%) |

* Blend of 80% standard gas oil with 20% vacuum tower bottoms.

Table 4

## MAT test results on fresh catalysts

| | No metals, low severity steaming | | | | No metals, high severity steaming | | | | 3,000 ppm Ni, 3,000 ppm V, resid containing feed | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst | "A" | "B" | "C" | "D" | "A" | "B" | "C" | "D" | "A" | "B" | "C" | "D" |
| Conversion, vol % | 78.4 | 78.4 | 78.6 | 78.7 | 69.7 | 66.5 | 71.0 | 72.0 | 60.8 | 64.3 | 66.5 | 71.7 |
| Yields: vol % | | | | | | | | | | | | |
| Total $C_3$ + $C_4$ | 25.0 | 25.3 | 25.9 | 24.6 | 20.6 | 18.9 | 21.8 | 21.7 | 15.6 | 16.6 | 16.1 | 19.0 |
| Iso/olefin ratio | 0.65 | 0.66 | 0.62 | 0.64 | 0.48 | 0.47 | 0.50 | 0.58 | 0.40 | 0.42 | 0.41 | 0.50 |
| Gasoline | 61.6 | 61.5 | 60.4 | 64.0 | 57.0 | 56.7 | 57.0 | 59.0 | 48.8 | 50.6 | 52.7 | 55.5 |
| LCO/D.O. ratio | 2.32 | 2.13 | 2.43 | 2.61 | 1.94 | 1.42 | 1.99 | 2.11 | 1.39 | 1.38 | 1.90 | 2.15 |
| Coke selectivity factor | 1.28 | 1.48 | 1.43 | 1.21 | 1.45 | 1.47 | 1.31 | 1.34 | 3.39 | 2.56 | 2.79 | 2.52 |

version vs. cat/oil curve is greater at lower cat/oil ratios than at higher ones.

In addition, the temperature sensitivity of the test is greater at lower cat/oil ratios. This indicates that a lower cat/oil ratio test is more sensitive to differences between catalysts—at least at the conversion levels obtained with these samples.

A major objective of the study was to define MAT and steam deactivation conditions that would result in selectivities similar to those seen in commercial operations. To accomplish this, it is important to choose conditions which will result in the correct ratio of catalytic to thermal cracking.

One of the primary differences between catalytic cracking reactions and thermal conversion is the ratio of saturated/unsaturated products that are generated. Therefore, one simple indicator of the type of reactions taking place is the weight ratio of isobutane/($C_3$ + $C_4$) olefins.

This quantity is almost always measured in commercial operations and can easily be obtained in a standard MAT evaluation. By examining numerous commercial operations, it was found that this ratio was usually between 0.15 and 0.45, and was a function of reaction temperature, cat/oil ratio, contact time, and of course, catalyst activity and type.

Fig. 4 illustrates the effects of cat/oil, temperature and space velocity on iso/olefins ratios for fresh catalysts. A typical range of commercial iso/olefin ratios is shown.

As expected, the iso/olefin ratio increases with a decreasing reaction temperature and space velocity and with increasing cat/oil ratios since these conditions favor catalytic cracking over thermal cracking. However, none of the runs at any combination of conditions fell within the range of typical commercial iso/olefin ratios.

This indicates that the steam deactivation conditions used in this case (1,450° F., 2 hr) were not sufficiently severe to bring the catalyst activity (and consequently the iso/olefin ratios) into the typical commercial operating range.

Fig. 5 illustrates the effects of MAT conditions on iso/olefin ratio with equilibrium catalyst. The trends are the same as with the fresh catalyst, except that the entire range of iso/olefin ratios shifts downward to an area more or less within that of the commercial refinery runs.

At the higher cat/oil ratios, the lower reaction temperatures resulted in iso/olefin ratios that were outside the commercial range, even with the equilibrium catalyst. Further, the entire range of iso/olefin ratios at the higher space velocity were more typical of the commmercial refinery data than were those at the lower space velocity. Thus, higher space velocities and higher temperatures more closely matched commercial selectivities than the conditions (900° F., 16 WHSV) that are currently recommended in the ASTM MAT procedure.

The study results lead to a detailed examination of the steaming conditions necessary to deactivate a fresh catalyst. Steam deactivation conditions must be representative of commercial deactivation to allow true catalyst differences to be reflected in the MAT evaluations, and must be accomplished in a reasonable time and manner.

A family of steam deactivation curves for a typical FCC catalyst is shown in Fig. 6. The shape and placement of this family of curves may shift, depending upon the catalyst type.

Thermal shock procedures (vs. a gradual warm-up) were used to simulate the catalyst's introduction to a commercial FCCU. Fig. 7 shows the conversion vs. steaming time at various temperatures. Figs. 6 and 7 illustrate the need for accurate time and temperature control.

A time difference of 5 min or a temperature difference of 4° F. translates to a conversion delta of as much as 5 points, taken at the inflection point. Thus, accurate control is essential.

Illustrated in Fig. 8 is the effect of the steam deactivation temperature on iso/olefin ratio at constant MAT conditions of 32 WHSV and 3.0 cat/oil. The range of commercial iso/olefin ratios is also shown. The data describe a typical transition from predominantly zeolite activity to predominantly matrix activity as steam deactivation temperature increases.

Steaming and metals-loading conditions must be chosen with care to match the severity of the commercial operation. One method is to evaluate a given unit's fresh catalyst and vary loading and steaming conditions until the treated fresh catalyst matches the activity and selectivity of the equilibrium catalyst from the same unit. One could then use these steaming conditions at constant metals loadings to predict the performance of various other catalysts in that commercial unit.

Of course, care must be taken when comparing catalysts with an active matrix to those with little or no matrix activity. In general, the catalysts with matrix activity will require different steaming conditions (i.e., longer times at lower temperatures) to match commercial equilibrium selectivities.

**Guidelines.** The subject of evaluating FCC catalysts is very complex. Nevertheless, there are some conclusions that can be drawn and some guidelines that should be followed in evaluating fresh FCC catalysts.

- Careful design and accurate control of steam deactivation equipment are critical elements in obtaining consistent steaming results. At high severity conditions, deviations of 2-4° F. can affect conversions by as much as 5 wt %. In addition, the designs of the various microactivity components are extremely important in achieving consistency, accuracy, and flexibility in MAT evaluations.
- Physical and chemical analyses provide excellent clues which help explain a catalyst's behavior. Key ana-

lyses include: alumina type and content, pore size distribution, zeolite unit cell dimensions, rare earth content, sodium content, and surface area.

- Definition of the proper steam deactivation conditions is vital in correlating MAT data with commercial catalyst performance. Conditions should be set so that deactivated catalysts match commercial equilibrium samples both in activity and selectivity. For a 2-hr steaming, at atmospheric pressure and 95% steam, temperatures between 1,500 and 1,535° F. accomplish these objectives.
- For MAT evaluations at 3.0 cat/oil ratio, space velocities and temperatures should both be higher than the ASTM levels of 16 WHSV and 900° F., respectively, in order to better simulate commercial selectivities. Levels of 32 WHSV and 960° F. are recommended. The results from this paper have been shared with the ASTM D-32 committee to help in defining new standard MAT test conditions.
- Several microactivity tests are required to characterize catalyst performance. Testing after mild steam deactivation defines inherent catalyst activity and selectivity. Testing after severe deactivation determines stability, and evaluation after metals impregnation with a resid containing feedstock demonstrates metals tolerance and heavy oil cracking ability.

Work is proceeding with the ASTM D-32 committee to develop a standard MAT test for evaluating resid cracking catalysts.

- Finally, it must be recognized that the methods discussed are not sufficient to completely evaluate FCC catalysts. These results must be combined with pilot plant results on commercial equilibrium samples and with reliable commercial test run results to get a complete picture of catalyst performance. The subjects of pilot plant and commercial testing will be covered in future articles.

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**Refining Technology**

# Commercial usage for new Japanese conversion catalyst

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Effective resid conversion has been demonstrated by partially replacing conventional resid catalyst in a modified commercial hydrodesulfurization (HDS) unit with a new HDS catalyst, R-HYC. With feedstocks containing 65-75% of 1,000° F.$^+$ residue, 60% conversion of the 1,000° F.$^+$ material was achieved during operation for more than 6,000 hr at 85-90% desulfurization.

Product properties satisfied the specifications for commercial use. Economics of the R-HYC catalyst application to a conventional HDS unit were studied for two feedstocks: Kuwait and Murban atmospheric residues.

Based on a paper presented at the American Petroleum Institute 51st Midyear Refining Meeting, San Diego, Calif., May 12-15.

Table 1

## R-HYC 4 catalyst properties

| | |
|---|---|
| Carrier | Zeolite-alumina |
| Supported metal | VI and VIII group metals |
| Shape | Extrudate |
| Size | $^{1}/_{16}$-in. diameter |
| Apparent bulk density, g/ml | 0.5 |
| Compact bulk density, g/ml | 0.6 |
| Surface area, sq m/g | 400 |
| Crush strength, kg/mm | 1.0 |

Table 2

## Properties of feedstock and product

| | — Feed — | | — Product — | |
|---|---|---|---|---|
| | Kuwait AR | Naphtha | Middle distillate | Residue |
| Gravity, °API | 13.3 | 53.2 | 32.8 | 17.2 |
| Sulfur, wt % | 4.24 | — | 0.03 | 0.96 |
| Nitrogen, ppm | 2,100 | 4 | 6 | 1,820 |
| Concarbon residue, wt % | 12.4 | — | — | 10.1 |
| Vanadium, ppm | 54 | — | — | 4.1 |
| Nickel, ppm | 17 | — | — | 5.4 |
| Pour point, °F. | — | — | −9 | — |
| Cetane index | — | — | 47 | — |

Because of the recent significant shift to nonpetroleum energy sources and stimulated energy conservation, the petroleum products market is limited, and the price of petroleum products has fallen.

The demand for residual fuel oil will continue to decline while the demand for gasoline and diesel fuel will stay almost constant. Thus, attention must be paid to resid conversion.

Idemitsu Kosan Co. Ltd. started developing the resid hydrocracking process (R-HYC process) in 1979 as a member of the Research Association for Residual Oil Processing (Rarop), sponsored by the Japanese government, and developed a new generation of catalysts (R-HYC) for the process.

Idemitsu Kosan Co. Ltd. has four conventional resid HDS units and has looked for effective ways to utilize these resid HDS units for converting residual oil to lighter products. Through test operations using one of these units, R-HYC catalysts combined with conventional HDS catalyst have demonstrated their capability to produce excellent distillates as well as low-sulfur and low-metal fuel oil.

**Catalyst.** To realize significant production of distillates (naphtha and middle distillates) from residual oil using a fixed bed process, the catalyst is required to meet the following requirements:

- High activity to crack heavy residues selectively to desired smaller hydrocarbons
- High hydrogenation activity in optimum combination with cracking activity
- High tolerance to contaminants in feedstocks such as metals and coke precursors.

For this objective, the development of the R-HYC catalysts was carried out through extensive catalyst screening, pilot plant runs, and engineering studies at our central research laboratories during 1979-1985.[1]

Idemitsu's new generation of catalyst (R-HYC 4) satisfies the above requirements, and its performance has been demonstrated in a commercial HDS unit at Idemitsu. Because of the novel composition of the zeolitic catalyst, R-HYC 4 can sustain its high hydrocracking activity and high selectivity to naphtha and middle distillates for the period of commercial operation, and has high desulfurization, demetallation, and deasphalting activities as well as hydrocracking activity.

Table 1 and Fig. 1 show the typical properties and performance of R-HYC 4. Table 2 shows the properties of feedstocks and products of pilot plant runs.

Product properties satisfy the specification for commercial use, without any down-stream hydroprocessing.

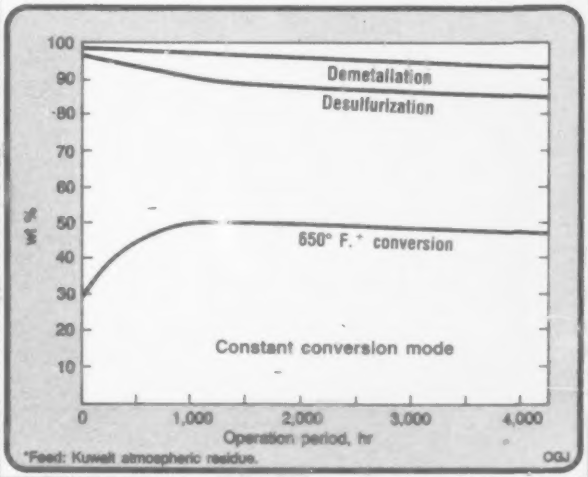
Regarding investment strategy, it is obvious that replacement of a portion of the conventional HDS catalyst with R-HYC 4 will be attractive for the refiner who has a resid HDS unit, to achieve resid conversion with minimum investment. Usually, the amount of catalyst replacement will be limited by the design of the existing unit, such as the reactor quenching system and product fractionation capability.

An average performance of R-HYC 4/conventional HDS catalyst for a 1-year operation was estimated based on the pilot plant runs with Kuwait atmospheric residue as a feedstock. At 50% R-HYC 4 inventory, 650° F.+ conversion was increased by about 10% as compared to a conventional HDS catalyst (Fig. 2).

Generally, sulfur content in the bot-

Fig. 1

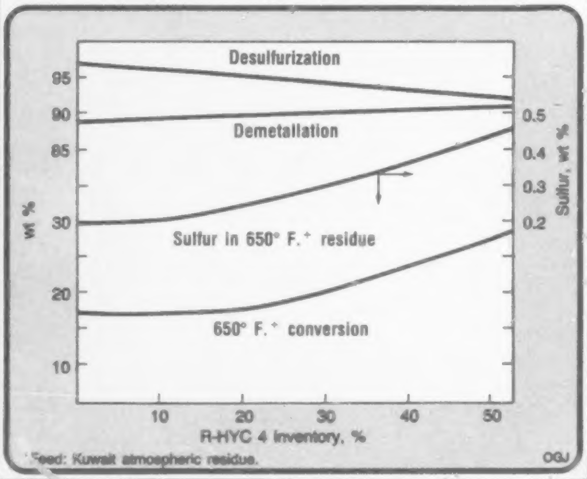
## Performance of R-HYC 4 catalyst



*Feed: Kuwait atmospheric residue.

Fig. 2

## R-HYC/HDS catalyst performance



*Feed: Kuwait atmospheric residue.

Table 3

## Average properties of feedstocks

| | Average | Range |
|---|---|---|
| Gravity, °API | 11.5 | 8.8-13.3 |
| Sulfur, wt % | 3.8 | 3.4-4.1 |
| Nitrogen, ppm | 2,750 | 2,200 - 3,100 |
| Concarbon residue, wt % | 16.9 | 16.0-18.3 |
| V + Ni, ppm | 118 | 85-155 |

Table 4

## Product properties for demonstration

| | Naphtha | Middle distillate | Heavy gas oil | Residue |
|---|---|---|---|---|
| Gravity, °API | 59.5 | 28.4 | 25.5 | 7.1 |
| Sulfur, wt % | 0.007 | 0.01 | 0.16 | 0.92 |
| Nitrogen, ppm | 30 | 239 | 478 | 2,650 |
| Concarbon residue, wt % | — | — | <0.01 | 13.2 |
| V + Ni, ppm | — | — | <1.0 | 20 |

toms product slightly increases as R-HYC 4 inventory increases. Although R-HYC 4 shows higher demetallation content activity than conventional HDS catalyst, metal content in the bottoms product is about the same as with conventional HDS catalyst. In the case of Kuwait atmospheric residue, the bottoms product with less than 50% inventory of R-HYC 4 would be suitable for feedstock to the resid fluid catalytic cracking (FCC) unit.

**Commercial application.** The first commercial application of R-HYC catalyst was R-HYC 1/conventional HDS catalyst in one of Idemitsu's refineries. The test was carried out in 1982, and its experience was reported previously.[2,3] Since the first application, three other R-HYC catalysts were tested in commercial operations: R-HYC 2 in 1983, R-HYC 3 in 1984, and R-HYC 4 in 1985. The main objectives of these test programs were to prove:

- The performance of R-HYC catalysts manufactured industrially by a Japanese catalyst manufacturer.
- The performance of R-HYC catalysts/conventional HDS catalysts.
- The operability and safety of the modified commercial unit.

Fig. 3 presents a simplified process flow scheme of the modified commercial unit, which was originally designed for low-sulfur fuel oil production with as low a conversion as possible.

Before the test operation with R-HYC catalyst/conventional HDS catalyst, the original process design needed to be changed based upon the analysis of pilot plant data to be in accordance with R-HYC catalysts performances.

Main modifications were more in regard to:

- Safety system, such as reactor temperature monitoring system and emergency system. Hydrogenation activity of R-HYC catalysts is higher than that of conventional HDS catalyst which results in faster temperature rise for R-HYC catalysts than that for conventional HDS catalyst under unusual conditions such as emergency stop of the hydrogen compressor. Thus the original design was thoroughly checked, and necessary reinforcement or change of the system was made.
- Pumps, heat exchangers, piping, and instruments, etc. of fractionation section because of the insufficient capacity due to the lower conversion in the original design.

Generally, the degree of modification must be a trade-off between the required investment and the amount of R-HYC catalysts. Overall economics, including several other factors, must be considered for an actual application.

Demonstration programs with the commercial HDS unit have been carried out with 25% R-HYC 1/75% conventional HDS catalyst in 1982, and with 25% R-HYC 2/75% conventional HDS catalyst in 1983, to confirm the activity, selectivity, and stability of each catalyst. During 1984 and 1985, the amount of R-HYC catalysts was increased to 50%, and from the start-of-run the reaction temperature was raised high enough for as high a conversion as possible, based on the demonstration experience obtained in 1982 and 1983.

The feedstocks for the demonstration varied from relatively low-metal (89 ppm) and low-Conradson carbon (15.9%) residues to very high-metal (154 ppm) and high-Conradson carbon (18.3%) residues. A wide variety of mixtures of atmospheric residues from 12 kinds of crude oils was used, but always included pitch from the propane deasphalting unit.

Table 3 shows the average properties of varied feedstocks far heavier than Kuwait atmospheric residue.

In 1985, with these very heavy feedstocks the demonstration with

Fig. 3

Flow diagram of modified HDS unit

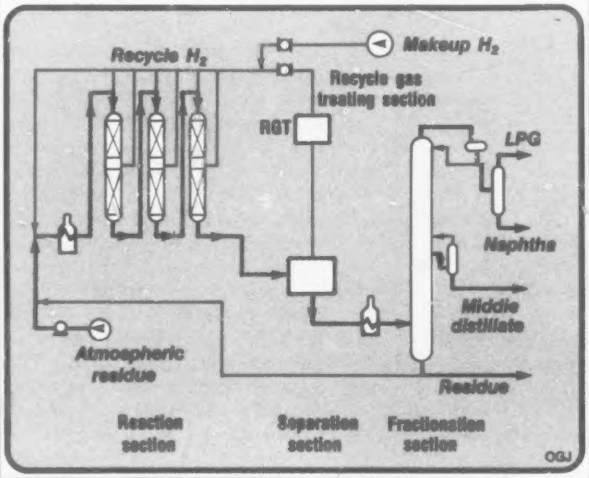
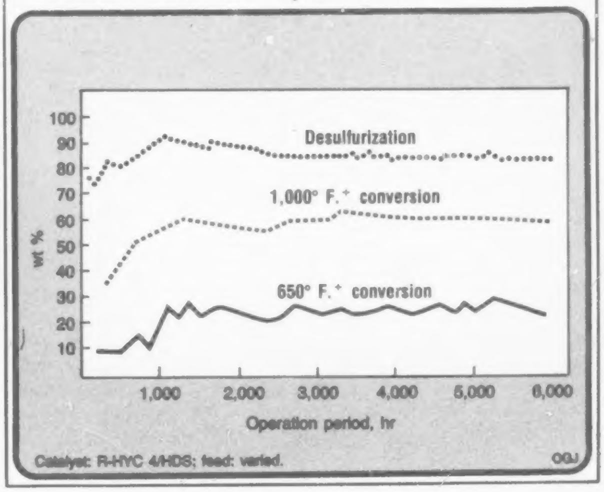


Fig. 4

Demonstration operation



Catalyst: R-HYC 4/HDS; feed: varied.

Table 5

## Atmospheric residue properties

| | Kuwait | Murban |
|---|---|---|
| Gravity, °API | 13.3 | 17.0 |
| Sulfur, wt % | 4.24 | 2.22 |
| Nitrogen, ppm | 2,100 | 1,560 |
| Concarbon residue, wt % | 12.4 | 9.5 |
| Vanadium, ppm | 54 | 32 |
| Nickel, ppm | 17 | 12 |

Table 6

## Summary of case studies

| Case | Base-A | A-1 | A-2 | Base-B | B-1 |
|---|---|---|---|---|---|
| Process | HDS | R-HYC/HDS | R-HYC/HDS + R-FCC | HDS | R-HYC/HDS |
| Feedstock | KW-AR | ← | ← | MR-AR | ← |
| Feed rate | 50,000 b/sd | ← | ← | ← | ← |
| Product, b/sd | | | | | |
| Gas, 1,000 lb/d | 85 | 170 | 600 | 85 | 230 |
| $C_3$-$C_4$ | 350 | 550 | 8,150 | 300 | 800 |
| Naphtha | 2,200 | 4,050 | 4,050 | 2,550 | 6,800 |
| Gasoline | — | — | 20,700 | — | — |
| Middle distillate | 7,750 | 11,100 | 11,100 | 5,900 | 9,800 |
| LSFO* | 41,950 | 37,050 | 8,900§ | 43,800 | 36,000 |
| MSFO† | — | — | 2,800¶ | — | — |
| Coke, 1,000 lb/d | — | — | 790 | — | — |

*Low sulfur fuel oil; †medium sulfur fuel oil; §light cycle oil; ¶heavy cycle oil & decant oil.

50% R-HYC 4/50% conventional HDS catalyst was carried out without any operational problems for about 6,000 hr. Although enough catalyst activity remained for continued operation, the unit was shut down for scheduled maintenance. Fig. 4 shows the operational results.

Conversion stayed almost constant for the entire operation period; 25% of 650° F.⁺ conversion and 60% of 1,000° F.⁺ conversion were maintained, which was far higher than those with conventional HDS catalyst. Although desulfurization slowly went down with catalyst aging, it remained more than the planned target of 85% during the entire period. Demetallation stayed at the level of 80-90%, which was slightly higher than that with conventional HDS catalyst.

Table 4 shows typical product properties from the demonstration operation in 1985. Generally, properties are almost the same as HDS products.

Naphtha was superior to straight-run naphtha and was a suitable hydrotreater/reformer feedstock. The middle distillate was of good quality and used as blend stock for diesel oil production.

Heavy gas oil was fed to a fluid catalytic cracking unit for producing gasoline blend stock. The bottom product, which contains 50% of vacuum gas oil fraction (a good feedstock to a fluid catalytic cracking unit), was used as blend stock for low-sulfur fuel oil as usually done with conventional HDS catalyst operation.

With an existing resid HDS unit, part of the conventional HDS catalyst can be replaced by R-HYC catalyst to achieve a significant increase of excellent distillates, while maintaining the quality of the bottom product.

**Case studies.** Case studies were run on two different feedstocks: Kuwait atmospheric residue (KW-AR) and Murban atmospheric residue (MR-AR).

Base cases (base case A, KW-AR; base case B, MR-AR) using conventional HDS catalyst were compared to test cases as follows:

Case A-1: Combined with R-HYC 4/HDS, using KW-AR

Case A-2: R-HYC 4/HDS + resid FCC, using KW-AR

Case B-1: R-HYC 4/HDS, using MR-AR

A summary of the feedstock properties is shown in Table 5. Kuwait atmospheric residue is the same feed used in the pilot plant runs described previously. Murban atmospheric resid is from another typical crude oil in the Japanese oil industry and has higher hydrocracking activity than Kuwait on R-HYC 4 catalyst while remaining about the same reactivity as Kuwait on conventional HDS catalyst.

For all of these cases, the hypothetical unit chosen as the basis for the study was a conventional, 50,000 b/sd resid HDS unit. Average performances were estimated for 1 year of operation at the same hydroprocessing conditions, i.e., temperature, pressure, liquid hourly space velocity (LHSV), and hydrogen-to-oil ratio.

The results of the base case on Kuwait atmospheric resid show that the 4.4 vol % yield of naphtha would have to be hydrotreated for catalytic reformer feed but not for feed to ethylene production.

Middle distillate, at 15.5 vol % yield, is suitable for diesel fuel blending because of its high cetane number. As for the bottoms product, sulfur content was less than 0.3 wt %, and metals content was also less than 20 ppm.

In this case, 650° F.⁺ conversion was about 5% higher than the conventional HDS operation to keep a constant sulfur level during the entire operation. Total liquid production was 104.5 vol % and fuel oil production was reduced by 16 vol %.

Case A-1 used 50% R-HYC 4/50% conventional HDS catalyst. This replacement of the catalyst in the base case provided a 650° F.⁺ conversion increase of 9.7% compared to the base case. Gas and naphtha yields increased about 4%, and middle distillate increased about 7%.

Total liquids production was 105.5 vol %, and fuel oil production was reduced by 26 vol %. Properties of the naphtha and middle distillate are almost the same as those for the base case.

As for bottoms product, sulfur content increased to 0.44 wt %, and metals content remained almost the same, which indicates that the bottoms product is a suitable feed for the resid FCCU.

Case A-2 used the same catalyst mix as case A-1, but used a resid FCCU for upgrading Kuwait atmospheric residue, in which unconverted residue from the hydroprocessing unit was fed to the FCCU. This combination provided total liquids yield of 111.4 vol % and a middle distillate/total naphtha ratio of 0.45.

The use of R-HYC 4/HDS catalyst as a pretreatment step for the resid FCCU permits upgrading a wide variety of

Table 7

## Product prices*

| | |
|---|---|
| Gas | 4 $MMBTU |
| $C_3$-$C_4$ | 16.4 $/bbl |
| Naphtha | 29.8 $/bbl |
| Gasoline | 31.06 $/bbl |
| Middle distillate | 30.98 $/bbl |
| Light cycle oil | 30.52 $/bbl |
| Low sulfur fuel oil | 24.98 $/bbl |
| Middle sulfur fuel oil | 22.85 $/bbl |
| Coke | 66.14 $/1,000 lb |

*Base: U.S. Gulf Coast, 1985.

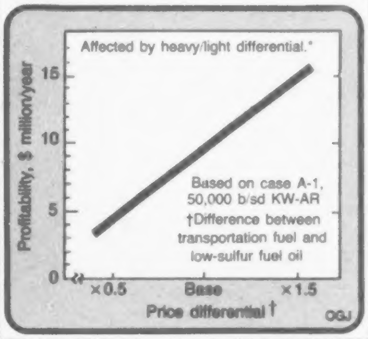
Table 8

## Economics analysis

| **Case** | **Base-A** | **A-1** | **A-2** | **Base-B** | **B-1** |
|---|---|---|---|---|---|
| **Feedstock** | **KW-AR** | | **KW-AR** | **MR-AR** | |
| **Scheme** | **HDS** | **R-HYC/HDS** | **R-HYC/HDS + R-FCC** | **HDS** | **R-HYC/HDS** |
| Product value, $/bbl | 27.30 | 28.22 | 32.58 | 27.28 | 28.71 |
| Revamping cost, $/bbl | — | (0.04) | (0.04) | — | (0.04) |
| Relative operating cost, $/bbl | — | (0.30) | (1.04) | — | (0.71) |
| **Total** | **27.30** | **27.88** | **31.50** | **27.28** | **27.96** |
| Profitability, $ million/year | 9.53 | | — | 11.17 | |

Fig. 5

## Profitability*



residual oils, and this is obviously attractive to the refiner that already has a resid FCCU as well as an HDS unit.

When results of the base case using Murban atmospheric resid were compared to the base case on Kuwait, gas and naphtha yields stayed almost at the same level, and 650° F.⁺ conversion was somewhat lower.

Total liquids production was 105.1 vol % and fuel oil reduction was 13 vol %. Sulfur content in the bottoms product was less than 0.1 wt %.

Case B-1 used 50% R-HYC 4/50% HDS catalyst. Catalyst replacement allowed 650° F.⁺ conversion to increase by about 15%—from 13% in the base case to about 28%. It must be noted that the middle distillate/naphtha yield ratio decreased to 1.4 compared to 2.3 for the base case.

This increase in conversion resulted in an increase of hydrogen consumption of 200 scf/bbl. Total liquids production was 106.8 vol % and fuel oil reduction was 28 vol %. The bottoms product, 0.18 wt % sulfur and 4 ppm metals, is also suitable feedstock for the resid FCCU.

Table 6 summarizes the feedstocks and products slates.

**Economics analysis.** The product prices used for the analysis are shown in Table 7. The average prices in the U.S. Gulf Coast during 1985 are used, and the price differential between transportation to fuel and low-sulfur fuel oil is about $6/bbl. Costs to upgrade naphtha to a gasoline blend stock are taken into account.

The capital investment required is assumed to be $5 million for modifications of an existing 50,000 b/sd HDS unit in order to use R-HYC 4 at 50% inventory, depending upon the degree of revamping required. Hydrogen is assumed to be available from an existing facility. Depreciation is calculated at 6.7% (15 year straight-line method), and 5% investment/year for maintenance, insurance, and taxes.

Relative operating costs for base-A and A-1 cases, and base-B and B-1 cases respectively, represent cost differentials between R-HYC/HDS and HDS units. For the A-2 case, relative operating costs are the cost differentials in the hydroprocessing section plus full operating costs in the resid FCC section.

The cost differentials between R-HYC/HDS and HDS units include hydrogen and catalyst costs. Other utility costs are not included because of little difference.

The price of R-HYC 4 is assumed to be $2.50/lb higher than conventional HDS catalyst, and hydrogen price is assumed to be $2.80/Mscf. The operating costs, $1/bbl, in resid FCC section include utility and catalyst costs.

Based on the estimated product slates, the assumed product prices, the relative operating costs, and the estimated investment costs for modifications, the following economics analysis is made.

As shown in Table 8, subtracting the revamping cost and relative operating costs from the product values provides a relative gross income for each case, and the profitability for catalyst replacement is obtained. This profitability ranges from $9.5 million/year for Kuwait atmospheric residue, to $11.2 million/year for Murban atmospheric residue.

Naturally, the profitability is a function of the transportation fuel/low-sulfur fuel oil price differential. In the above analysis, a $6.08/bbl price differential between gasoline and low-sulfur fuel oil, and a $6.00/bbl differential between diesel oil and low-sulfur fuel oil are assumed. Fig. 5 presents the sensitivity of the profitability to the price differential.

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### Acknowledgment

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# Dense-phase catalyst conveying successful in Australia

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Dense-phase catalyst conveying was successfully utilized at the Shell refinery in Geelong, Australia, on July 31, 1985. Approximately 28 cu m of a metallic catalyst with an alumina carrier were transported from the ground to the top of a 35-m reactor with no measurable loss of catalyst particle length.

**Process unit.** The hydroextraction unit (HXU) at the Geelong refinery is part of the lube-oil process and uses Shell's NTX-6 catalyst in a hydrotreating role. The catalyst is typically 1.5-mm diameter by 2 to 4-mm long.

The reactor is approximately 31 m in length and contains five beds composed of catalyst and support material. The overall lift required for the catalyst loading is 35 m.

**Catalyst loading.** The dense-phase catalyst loading system consists of a surge hopper, pressure chamber, transfer pipe, interceptor cyclone, and separation chamber. The catalyst was poured from its storage container (200-l. drums) into the surge hopper where a predetermined volume of catalyst is metered into the pressure chamber.

With the assistance of air, the catalyst was transported as a slug to the interceptor cyclone and separation chamber.

A negative pressure was maintained on the interceptor cyclone and separation chamber which enabled dust and fines removal from the catalyst prior to sock loading.

At the same moment the catalyst leaves the interceptor cyclone, another charge of catalyst fills the pressure chamber ready for transport. This allows a continuous supply of catalyst to the loading sock.

During the loading operation, checks were continually made to determine the average and peak transfer velocities. The average velocity was determined by timing the period of high air pressure, at the time of release from the pressure vessel, until air breakthrough occurs at the interceptor cyclone.

Average transfer velocities were consistent at 0.6 to 0.7 mps. Peak velocities attained by each slug were determined by timing the period of the slug's arrival, from front to end, as it reached the cyclone.

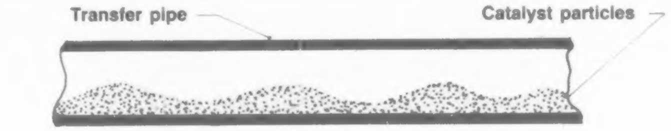
In this case, velocities up to 0.9 mps were reached.

Each slug averaged 60 sec/transfer which provided gross loading rates of 3.0 cu m/hr. Loading rates can be increased without an increase in transfer velocity by simply increasing the size of the dense-phase equipment.

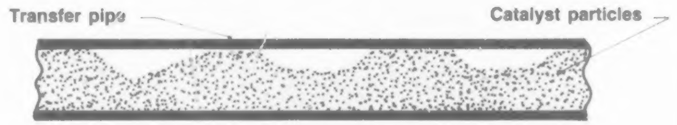
Sampling of catalyst was carried out regularly throughout the loading operation and consisted of samples taken prior to loading, and from the interceptor cyclone prior to fines separation. The samples were then compared for particle-size distribution and fines content.

Fig. 1

Catalyst flow modes



a. Lean-phase

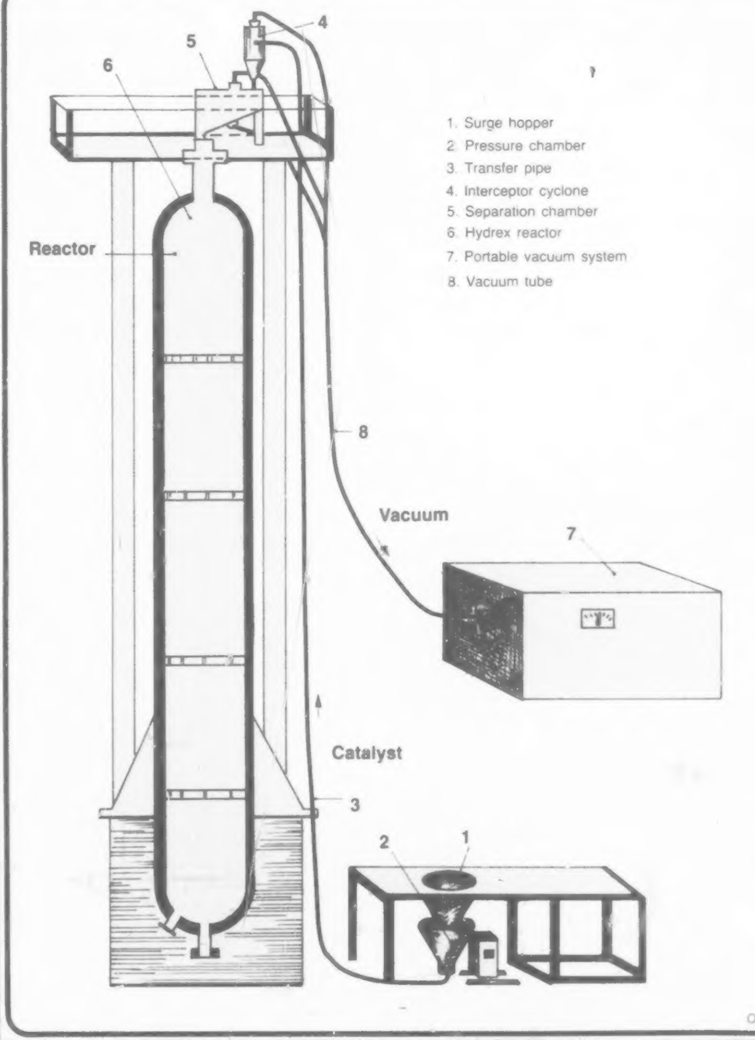


b. Dense-phase

OGJ

Fig. 2

Dense-phase loading system



OGJ

All samples taken were first seived to remove the very fine material, and two composite samples were constructed for the before-and-after cases.

Because the shape of the particle does not allow for length distribution analysis by a set of graded seives, a random selection of 100 particles was performed, and each particle individually measured.

The particles were selected by two methods.

First, a dip sample was taken, and second, a "coned-and-quartered" procedure was followed. Results from both methods are reported. Determination of catalyst granulometry via this procedure has previously been used at Geelong and had identified significant particle length reduction when other loading methods were used.

From the results in Table 1, it is clear that no significant reduction in particle length occurred; however, approximately 3 wt % of fine material was present. This fine material was most likely formed by the chipping of edges as particles collided during transport.

These small particles were removed by air washing from the interceptor cyclone and separation chamber prior to sock loading.

Further analysis of the samples indicated that the average particle length from two sampling techniques produced similar results. A "grab" sample produced an average length before loading of 1.99 mm, and 2.22 mm after loading. The coned-and-quartered sampling technique indicated that the average length was 2.25 mm before loading and 2.42 mm after loading.

## Technology

In order to better understand what was accomplished with the described job history, it is necessary to discuss conveying concepts in general. Developments in materials-handling systems have produced several different types of conveying systems.

**Negative-pressure system.** The negative-pressure type operates essentially by lean-phase fluidizing methods. A negative pressure is created in the system by a turbo exhauster or vacuum pump.

This produces a high-velocity air stream in which the conveyed material is entrained. The fluidized material is then rapidly conveyed along the pipeline until it tangentially enters a separator located above the receiving hopper.

**Lean-phase system.** The lean-phase system operates in a similar way to the vacuum system except that the air stream is now produced by positive

Table 1

### Sieve analysis of fresh NTX-6 catalyst*

| Particle size, mm | Before loading, % | After loading, % |
|---|---|---|
| > 1.18 | 99.40 | 96.46 |
| 1.18 – 1.00 | 0.48 | 1.66 |
| 1.00 – 0.85 | 0.06 | 0.58 |
| < 0.85 | 0.06 | 1.30 |

* 28 samples taken.

Table 2

### Catalyst conveying systems

| Type of system | Conveying velocity, m/min | Type of air supply required |
|---|---|---|
| Vacuum (Neg. pressure) | 900 to 1,500 | High volume, negative pressure |
| Lean phase | 900 to 1,500 | High volume, low pressure |
| Medium phase | 300 to 900 | High volume, low/med pressure |
| Dense phase | 36 to 300 | Low volume, high pressure |

pressure. Again, the material conveyed must disperse in the air stream to allow each particle to be pulled along.

If the air stream velocity falls below the minimum for the particular material being conveyed, drop out occurs.

Fig. 1a shows what typically happens inside the pipeline of a lean-phase system. This condition is sometimes called the "moving dune effect."

Because there is a great deal of fluidization of the material, there are considerable inter-particle and particle-pipe wall collisions. This, combined with the high conveying velocity, produces high pipe wear and material degradation.

Typical conveying velocities, depending on the material conveyed, are 900 to 1,500 m/min.

Very large quantities of low pressure (or negative pressure) air or gases are required.

**Medium-phase system.** The medium-phase system also relies on fluidization of the material in the air stream to achieve conveying. The air stream velocity is slower than the lean-phase system—in the range 300 to 900 m/min.

To ensure that the material does not drop out of the air stream, pipeline boosters are required which inject air along the pipeline to maintain material buoyancy.

Because of the relatively high conveying speed and the effect of pipeline boosters fluidizing the material, similar conditions to those shown in Fig. 1a exist within the medium-phase system.

High air-flow rates at low pressure are required for medium-phase systems.

**Dense-phase system.** The dense-phase system uses a low-volume, high-pressure air stream and relies on a continuously expanding volume of air pushing a cohesive slug of material along the pipe. Fluidization is completely eliminated and since the conveying velocity is also low, very fragile and difficult-to-handle materials can be conveyed.

Fig. 1b illustrates what typically happens in a dense-phase system. Material is no longer entrained in a high-velocity air stream. The material is pumped along in a controlled manner at low velocity using low-air volume.

Table 2 summarizes the different conveying systems.

The heart of the dense-phase, catalyst-loading system is the pressure chamber which has been specially designed to handle a wide range of catalyst sizes and shapes. The dense-phase mode of operation means that material contained in the pressure vessel is pushed into and along the pipeline by a continuously expanding volume of compressed air injected into the system at the pressure chamber.

The carefully designed vessel shape allows catalyst to be pushed into the pipeline without blockage. Transfer between the pressure vessel and pipeline is smooth because of the special outlet bend profile.

The equipment used to control the input of compressed air into the pressure vessel is an electropneumatic control system that allows the operator to modify and control catalyst feed rates and velocities to suit the type of catalyst being conveyed.

A specially designed valve is used to control the input of material into the pressure chamber.

This valve has the capability of shutting off the catalyst feed when the pressure vessel is full, and achieve an airtight condition, all in one simple action.

The pressure chamber fills from a gravity-supply surge hopper while the valve on the pressure vessel is open. The valve is open long enough to ensure a full vessel.

The valve then closes and high-pressure air enters the vessel, pushing the catalyst into and along the transfer piping in the form of a plug. The plug is conveyed to the interceptor cyclone and separation chamber.

A negative pressure is maintained on the cyclone and separation chamber at all times to remove airborne catalyst dust.

The separation chamber contains an appropriately sized vibrating screen to allow removal of catalyst dust and fines. Once the catalyst leaves the separation chamber, loading is accomplished by conventional methods.

A diagram of the loading system is shown in Fig. 2.

**System advantages.** Apart from the more obvious advantages of catalyst dust and fines removal, there are benefits relating to costs, space requirements, versatility, and the environment.

The most obvious cost-related consideration is the elimination of expensive crane hire.

The larger or taller the reactor, the greater the cost savings. Due to the simplicity of this loading system, labor requirements may be reduced by 20 to 30% over conventional loading methods.

Most plant shutdowns are scheduled along with project and inspection work and, hence, the job site becomes a very busy place.

Since the system requires little space, and less labor to operate, work safety is enhanced by fewer people with better access.

In cases where multiple reactors require simultaneous loadings, additional dense-phase units may be utilized.

The versatility of the dense-phase-loading technique is realized by its ability to change the dynamics of the system to suit the type and properties of the catalyst involved. This means that the same equipment can be used for fragile catalysts on a plant-wide basis.

If reactors are equipped with permanently installed transfer pipes, preparation work prior to reactor loading is minimal.

Catalysts must be protected from moisture during loading. By constructing weather protection above the surge hopper and reactor manway, catalyst loading may continue in most weather conditions. Either dry air or nitrogen may be used as the transport gas.

The dense-phase, catalyst-loading system offers an alternative to conven-

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tional catalyst loading techniques. The greatest advantages for the system exist where catalyst inventories are large and where tall reactors are installed.

Continuous regeneration Platforming, hydrocracking, desulfurizing, and sulfuric acid converters are examples of catalytic processes and reactors which would be candidates for the loading system. ▪

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# Alumina absorbents effectively remove HCl from reformer $H_2$ gas streams

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A particular operating problem in catalytic reformer operation involves the presence of contaminant chlorides in the hydrogen off gas. The chlorides ultimately lead to corrosion and ammonium chloride salt formation in downstream compressors and fuel-gas systems.

The problem can be solved quite efficiently and economically by processing the reformer gas through a fixed bed of alumina adsorbent.

The extensive surface structure of an activated alumina exhibits a very high affinity for chlorides. Therefore, it functions well in removing HCl so that effluent chloride levels of less than 1 wt ppm are achievable in properly designed adsorbers.

**Catalytic reforming.** The predominant catalytic reforming reactions are dehydrogenation and isomerization. Reforming catalysts in use today typically contain platinum or a combination of rhenium with platinum supported on an alumina base.

The platinum functions to catalyze dehydrogenation reactions, whereas, the alumina provides the necessary active sites for the isomerization reactions. In order to enhance isomerization, the catalyst is continually doped by adding chlorides to make the alumina sites more acidic.

A controlled injection of an organic chloride compound and water at the reformer reactor inlet restores the surface acidity of the catalyst and ensures good isomerization activity.[1,2]

Unfortunately, chloride loss from the reforming catalyst occurs slowly, but continuously, due to the possible hydrolysis of organic chlorides with water. This results in HCl.

The generated HCl then becomes a component of the hydrogen leaving the reformer and may also contaminate the liquid reformate. The potential for severe corrosion and salt formation will frequently justify a chloride removal unit of some type.

The newer continuous catalytic reforming processes (CCR) are susceptable to the chloride contamination problem. The catalysts employed seem to require higher levels of chloride addition for regeneration which compounds the problem of higher levels of HCl in the $H_2$ offgas.

Table 1

### $H_2O$ increases aluminas' capacity for chloride

| | Chloride water concentration, % | | |
|---|---|---|---|
| | 0.1 | 0.01 | 0 |
| **Type** | | | |
| A-201 3×6 m | 9.4 | 4.6 | 4.5 |
| A-201 5×8 m | 10.0 | 5.7 | 5.1 |
| A-201 ½×¼ in. | 8.8 | | |
| **Other commercial aluminas** | 8.8 | 5.0 | 4.5 |
| A-203Cl 3×6 m | 14.1 | 9.0 | 9.0 |
| 5×8 m | 15.7 | | |
| A-201/$NaAlO_2$ 3×6 m | 12.1 | 7.2 | 6.0 |

Test conditions: $N_2$ carrier gas with 0.1% HCl, ambient pressure and temperature, time of test—2 weeks, chloride results expressed as % in alumina at end of test.

**Chloride adsorption.** Activated alumina adsorbents are transitional aluminas of the chi-rho-eta ($\chi$-$\rho$-$\eta$) phase that are characterized by an extensive internal surface area of approximately 325 sq m/g. The important active sites on the alumina surface are either negatively charged oxygen, or hydroxyl ions and positively charged aluminum sites.

The sites are highly polar and, therefore, have a great tendency to adsorb polar molecules. In general, molecules with high dipole moments (high polarity) are more readily adsorbed by the alumina than nonpolar compounds.

Hydrogen chloride is quite polar (dipole moment of 1.08 Debyes) which accounts for the alumina's high affinity for removing HCl from the nonpolar hydrogen gas. In fact, the attraction for HCl molecules is so strong, the adsorptive mechanism is likely one of dissociation of the HCl molecule. The positively charged proton and the negatively charged chloride may dissociate and align with the oxygen and the aluminum sites, respectively.

The use of alumina in removing chlorides is not unique to hydrogen gas systems. Hydrocarbon streams with varying molecular weights can be scrubbed free of chlorides by processing the gas through an activated alumina bed. Due to their nonpolarity, most hydrocarbon systems provide very little competitive adsorption with the HCl molecules.

Chloride adsorption with alumina is

Table 2

## Smaller particle sizes adsorb more chloride

| Sample | Type | Chloride adsorbed, wt % | GHSV, hr$^{-1}$ | Hydrogen flowrate, MMscfd |
|---|---|---|---|---|
| 1 | A-201, 5 × 8 mesh | 6.3 | 154 | |
| 2 | A-201, 5 × 8 mesh | 9.8 | 127 | 29 |
| 3 | A-201, 1/4 × 8 mesh | 5.3* | 176 | 82 |
| 4 | Alumina, 5-10 mm | 3.7 | 61.4 | 30 |
| 5 | Alumina, 5-10 mm | 5.1 | — | 10 |

*Bottom adsorber sample only.

also possible in liquid system. For example, contaminant chlorides in liquid reformate or naphthas can also be removed by alumina adsorbents.

However, the capacity for chlorides is not as great in comparison to gaseous systems. Also, the adsorbent particle size is more critical to performance since mass transfer limitations are significant and, therefore, the use of smaller adsorbents is recommended.

**Experimental tests.** Experimental tests were undertaken to investigate, in depth, the performance of various alumina types in chloride-removal service. The aluminas used in the analysis were A-201 and A-203 (Cl) aluminas both manufactured by Kaiser Chemicals.

The A-203 (Cl) material is a promoted alumina that, as the data show, exhibits a much higher capacity for chlorides.

In order to demonstrate the alumina's capacity to adsorb chlorides, a thermogravimetric (Cahn) balance was set up to follow small weight changes of the alumina due to chloride pickup as a function of time.

Results of the tests for various HCl concentrations are shown in Fig. 1. Although the HCl concentrations used in the experiments are higher than typically experienced in reformer off gases, the data are useful for assessing the chloride capacity of the alumina.

The curves of Fig. 1 indicate that the adsorption rates are slightly concentration dependent. However, both curves are tending towards the same maximum capacity which implies that the partial pressure of HCl does not have a major effect on the ultimate capacity of the alumina, but does affect the rate of adsorption. This information is particularly important when sizing chloride adsorption vessels.

The time function in Fig. 1 was plotted on a log scale because the adsorption rate was very fast initially but then declined rapidly with time. Equilibrium adsorption capacities were not reached after 100 hr although adsorption rates had declined significantly.

A comparative evaluation of the rate of HCl adsorption by the improved adsorbent A-203 (Cl) was made, and the results are shown in Fig. 2. The rate of HCl adsorption is seen to be significantly greater for A-203 (Cl) than A-201. After a 90 hr exposure to the 0.1% HCl, the respective chloride contents were 12.1 and 7.1 wt %. These chloride levels are not final equilibrium values.

**Pilot testing.** To further simulate actual operating conditions, pilot column tests were set up to investigate adsorbent capabilities under dynamic conditions. A carrier gas containing low HCl concentrations was fed through a fixed column of alumina for an extensive period of time so that the alumina was allowed to adsorb a significant quantity of HCl.

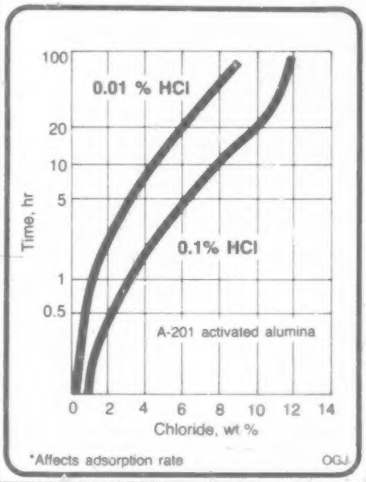
The use of sample ports throughout the length of the column showed that the adsorption front was relatively broad indicating a large mass transfer zone. It was also determined that while the front was moving down through the bed, some chloride was still being adsorbed at the top of the bed.

Because the mass transfer zone is quite large, it is important to size vessels for commercial use so that the length-to-diameter ratio (L/D) is as large as possible. Commercial experience has shown that L/D ratios of less than 2 fail to utilize the adsorbent charge efficiently. In fact, L/D ratios should be greater than 2.5 and preferably 3 or greater.

**Influence of water.** The hydrogen off gas from a catalytic reformer typically contains 15 to 20 vol ppm of water in addition to the 2 to 4 vol ppm HCl. Traditional thinking has been that the presence of $H_2O$ would actually lower the capacity of the alumina to remove chlorides as a result of competitive adsorption between $H_2O$ and HCl molecules for the active sites. The opposite is true.

Fig. 1

### HCl concentration*



*Affects adsorption rate

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Operation of the pilot columns has shown that the presence of $H_2O$ actually increases the alumina's capacity for chloride as the $H_2O$ concentration is increased.

Table 1 presents data that show how the alumina chloride capacity actually increases with moisture content. The chloride capacity doubled as the moisture content increased from 0 to 0.1%.

Based on this information, it is concluded that water does not retard or reduce the adsorption of HCl by alumina-based adsorbents. However, it is not clear whether the increased chloride level in the presence of water is a final capacity effect or whether it is simply a rate effect whereby the water acts as a catalyst.

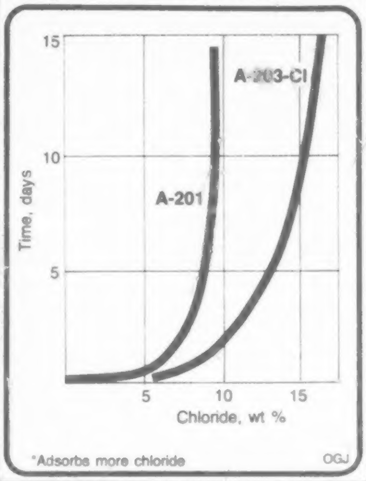
**Particle size effect.** The relative performance of the aluminas showed some interesting trends (Table 1). For a fixed type of alumina (A-201), the adsorption capacity was sensitive to particle size.

The capacity for the large size (½ × ¼, 8.8%) was less than the 3 × 6 mesh at 9.4% which was lower than the 5 × 8 mesh at 10.0%. This further tends to confirm some form of diffusional restriction.

However, the adsorption capacity for the improved, promoted A-203 (Cl) was even higher at 15.7% for the

Fig. 2

## Improved alumina*



*Adsorbs more chloride

5 × 8 mesh size. It is therefore recommended that smaller particle adsorbent sizes be used, provided pressure drop limitations don't exist.

The size effect is further demonstrated by the data shown in Table 2 which present information on spent samples from existing commercial units. All of these units operated with a standard activated alumina adsorbent and the smaller 5 × 8 mesh material exhibited higher capacities than the ¼ × 8 mesh material, which was still higher than the larger 5-10 mm alumina.

The capacity of a standard alumina (A-201 type) is limited to the 6-8% range for design purposes (Table 2). In other cases, it has been shown that the promoted alumina, A-203 (Cl), is capable of a 12 to 14% capacity which will result in either an extended bed life for existing units, or smaller vessel sizes for new installations.

**Adsorber design.** Based on data developed from operating pilot columns, along with information gathered from commercially operating chloride adsorbers, some general guidelines have been developed for sizing chloride adsorption units.

1. Due to the existence of a broad mass transfer zone as the chloride concentration front moves through the adsorber, the bed's L/D ratio should be as large as possible. L/D ratios should not be less than 2 and, if possible, preferably greater than 3. The bed sizing becomes a balance between pressure drop and L/D ratio.

2. A gas hourly space velocity (GHSV) based on actual flow conditions can range from 40 to 400 $hr^{-1}$. It is recommended that space velocities fall between 80 and 200 $hr^{-1}$.

3. The Reynolds number based on the adsorbent particle diameter, $DpV\rho/\mu$, should be greater than 50 to ensure adequate turbulent flow in a packed bed.

Table 3

## Typical chloride adsorptive design capacities

| | Capacities, lb chloride/100 lb alumina | |
|---|---|---|
| | Gas service | Liquid service |
| Activated alumina (A-201) | 6-8 | 4-6 |
| Promoted alumina (A-203 Cl) | 12-14 | 8-10 |

4. The smallest particle sizes should be utilized provided the pressure drop is tolerable. Because of diffusional limitations, the use of smaller adsorbent particles is recommended. In liquid systems, this criteria becomes even more important since the differential in chloride adsorptive capacity is even greater.

5. Table 3 shows some typical chloride adsorptive design capacities to be used when sizing adsorption beds. Note how the capacities are derated in liquid service.

Bed channeling and adsorbent fouling are more prevalent in liquid systems and often cause capacities to fall below expectation. However, with ideal mass transfer conditions, higher capacities can be achieved.

It was clear in all the studies that there is a severe rate restriction on chloride removal, at least after the first initial amount 0-3%.

It is likely that, initially, HCl adsorbs on the Lewis acid-base sites on alumina. This has been noted for other acidic species such as $SO_2$ which is strongly adsorbed.[3] Furthermore, there is evidence of this in the literature.[4-6]

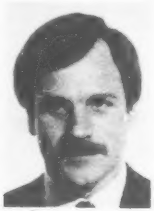
Peri has shown that the adsorption of $CO_2$, which normally occurs on these Lewis acid-base sites (or alpha sites), was completely inhibited by prior adsorption of HCl. He also noted that the chloride-alumina system is very complex and can involve free aluminum chloride or bulk oxychlorides in addition to simple adsorption.

It may well be some form of solid state chloride diffusion into the structure that is the rate-limiting step. In addition, the current work showed that chloride adsorption as a function of time was greater for smaller sized particles, thereby indicating diffusion or accessibility limitations.

It is clear that the smallest sized particle which is feasible should be recommended for commercial use. This also has an added advantage in that it gives maximum protection against fouling since it has been observed that the used plant samples were fairly heavily contaminated with carbonaceous material.

## The authors...

**Pearson**



**Janke**

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Pearson has authored a number of papers on aluminas in Claus catalysis. He holds BSc and PhD degrees in chemistry from the University of Leeds (U.K.).

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Previous assignments with Kaiser include process and project engineering positions. He holds a BS in chemical engineering from the University of California at Berkeley.

Because alumina adsorbents are relatively inexpensive in comparison to other adsorbent materials, beds are generally sized for 1 year service and, once saturated with chlorides, the adsorbent is dumped and the vessel recharged for another year's service.

Operation of a fixed-chloride adsorber is quite simple and trouble free. There are no moving parts to contend with, unlike other water wash or caustic treating systems employed for this service. The use of proper design guidelines when sizing vessels will result in efficient use of the alumina adsorbent and ensure that the effluent chloride concentration is essentially undetectable.

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# Tests show effects of nitrogen compounds on

Table 1

## Feedstock properties

| Feed no. | F-1 | F-2 | F-3 | F-4 |
|---|---|---|---|---|
| Gravity, °API | 22.0 | 22.8 | 24.4 | 28.1 |
| Sulfur, wt % | 1.19 | 1.06 | 0.93 | 0.47 |
| Nitrogen, wt % | 0.30 | 0.48 | 0.74 | 1.56 |
| Basic nitrogen, wt % | 0.094 | 0.16 | 0.37 | 1.23 |
| Conradson carbon, wt % | 0.12 | 0.1 | 0.07 | 0.01 |
| Aniline pt., °C. | 19 | 18 | 17 | 11 |
| Bromine no. | 12.3 | 16.6 | 18.1 | 28.7 |
| Refraction index at 67° C. | 1.4950 | 1.4911 | 1.4840 | 1.4700 |
| **Metals, ppm** | | | | |
| Fe | 4 | 3 | 2 | 2 |
| Ni | 0.6 | <0.5 | <0.5 | <0.5 |
| V | <0.2 | <0.5 | <0.5 | <0.5 |
| Cu | <0.1 | — | — | — |
| **Simulated distillation** | | | | |
| 10%, °C | 259 | 253 | 248 | 238 |
| 50%, °C | 393 | 381 | 367 | 328 |
| 95%, °C | 513 | 508 | 496 | 440 |
| Maximum °C. | 538 | 538 | 538 | 450 |
| UOP "K" factor | 11.5 | 11.5 | 11.5 | 11.6 |

**Julius Scherzer**
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Six commercial fluid catalytic cracking (FCC) catalysts have been evaluated for their resistance to the effects of nitrogen compounds on their performance.

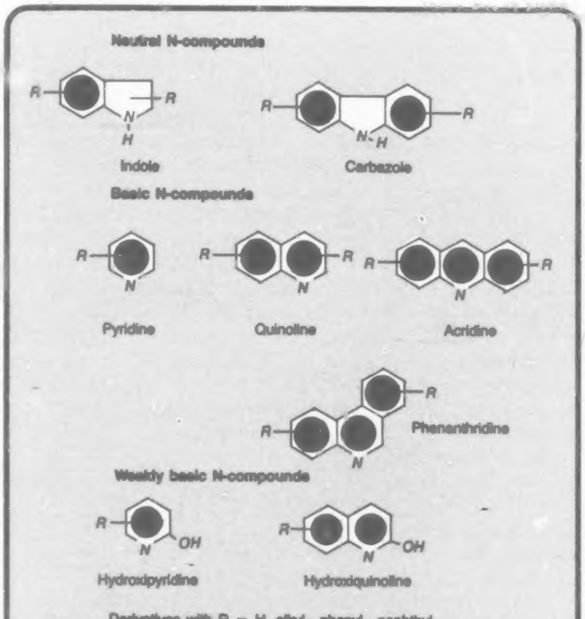
The results of the evaluations are important because of the shift in the quality of FCC feedstocks to heavier types containing higher levels of sulfur, metals, and nitrogen.

The impact of feedstock quality on the operation of FCCU's has been reviewed in several papers.[1] [2] The deleterious effects of nitrogen compounds on the performance of crack-

Based in part on a paper presented at the Katalistiks FCC Symposium, Venice, May 1986.

Fig. 1

Nitrogen compounds in crude oil[6]


Neutral N-compounds
R
R
N
H
Indole
R
R
N-H
Carbazole
Basic N-compounds
R
N
Pyridine
R
R
N
Quinoline
R
R
N
Acridine
R
R
N
Phenanthridine
Weakly basic N-compounds
R
N
OH
Hydroxipyridine
R
N
OH
Hydroxiquinoline

Derivatives with R = H, alkyl-, phenyl-, naphthyl-,

Nitrogen distribution in several Mid-East oils

Contents: 20-25% of nitrogen in 225-540° C. gas oil fraction.
75-80% of nitrogen in 540° C.+ vacuum resid fraction.
Type: 225-540° C. gas oil fraction: 50% of nitrogen as neutral nitrogen compounds, 33% as basic, 17% as weakly basic. 540° C.+ vacuum resid fraction: 20% of nitrogen in asphaltenes, 33% as neutral, 20% as basic, 27% as weakly basic.

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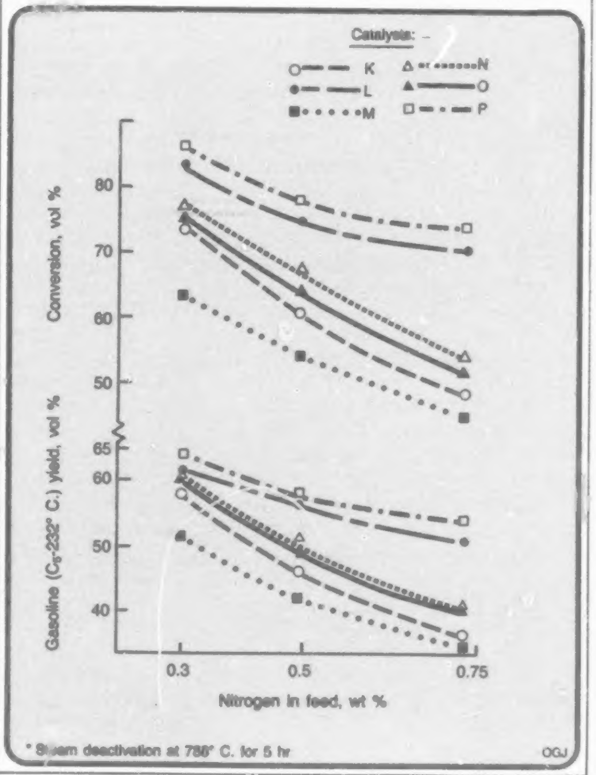
Fig. 2

Reduced conversion, gasoline yield*



* Steam deactivation at 788° C. for 5 hr

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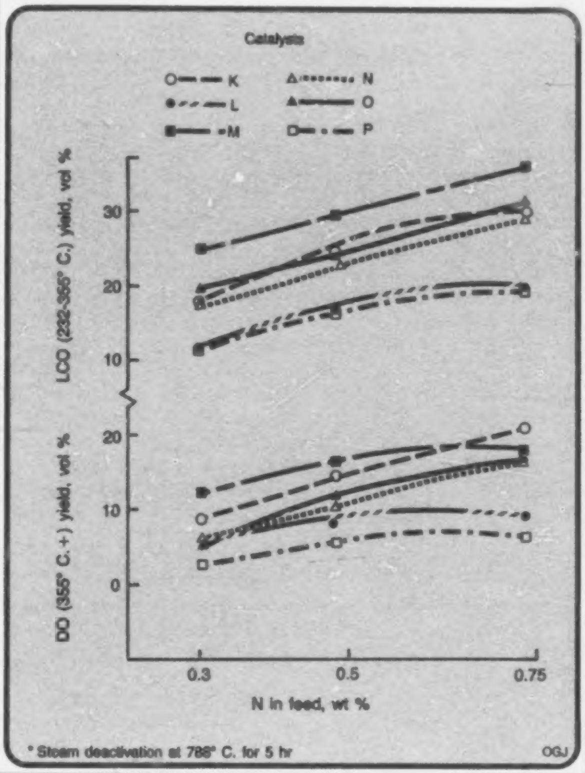
# commercial fluid cat cracking catalysts

Fig. 3

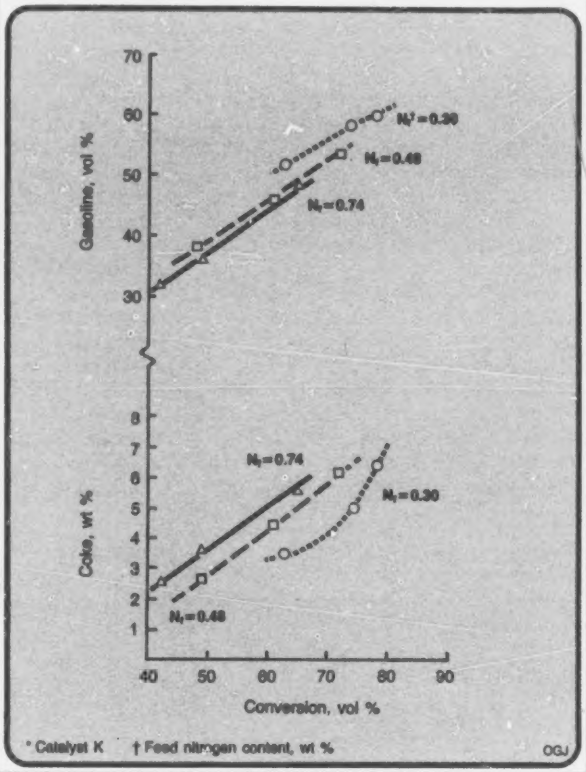
LCO and DO yields increase*



* Steam deactivation at 788° C. for 5 hr

Fig. 4

Gasoline and coke selectivities*



* Catalyst K † Feed nitrogen content, wt %

ing catalysts has been known for many decades.[3] [4] [5]

Significant progress has been made more recently in the identification and characterization of nitrogen compounds present in different oil fractions and feeds.[6] [7] [8] Furthermore, it was shown that hydrotreatment can significantly change the nitrogen-type distribution in a feedstock. Fig. 1 shows the different types of nitrogen-containing compounds found in petroleum fractions.

**Effects minimized.** Several approaches can be used to minimize the deleterious effects of nitrogen compounds during the catalytic cracking of high-nitrogen feedstocks:

1. Hydrotreating. This is a well-known technique used to decrease the nitrogen content in feedstocks. This process requires high pressures and temperatures.

2. Use of solid adsorbents for the removal of nitrogen compounds from feedstocks. The solid adsorbent is usually acidic and "captures" the basic nitrogen compounds. This method has been used to separate basic asphaltenes from feedstocks[11] [12] and for syncrude denitrogenation.[13]

3. Use of immiscible solvent to extract nitrogen compounds.[14] [15] [16] The method has been recommended to separate nitrogen compounds from shale oil.

4. Neutralization of basic-nitrogen compounds in feedstocks using acid additives. The products resulting from neutralization can be separated[16] or left in the feedstock.[17]

5. Use of nitrogen-resistant FCC catalysts. The major advantage of this method is elimination or greatly reduced cost of a pretreatment process.

**Post studies.** A number of papers have been published describing the cracking of model compounds over amorphous cracking catalysts[3] [4] and hydrogen Y-zeolites[18] [19] in the presence of various nitrogen-containing compounds. The relationship between the nitrogen content of an FCC feedstock and its effect on cracking catalysts has also been discussed in the literature.[20] [21]

In a recent publication, Fu and Schaffer[22] reported the effects of a variety of individual nitrogen compounds on the activity and selectivity of two commercial FCC catalysts. The authors found a correlation between the gas-phase proton affinity of the nitrogen-containing molecule and its poisoning effect on cracking catalysts.

Although the poisoning effects of different nitrogen compounds on cracking catalysts have been described in the literature, there is little information available with regard to the nitrogen resistance of different types of cracking catalysts. Nor are there any correlations between catalytic activity and the distribution of nitrogen (N) compounds in the liquid products and spent catalyst.

**Feedstocks.** We used a variety of feedstocks with different levels and types of nitrogen compounds. The properties of the feedstocks are shown in Table 1.

Feedstock F-1 is a vacuum gas oil (200 to 540° C. cut) similar to feedstocks used by California refineries. It contains about 0.3 wt % N. Two other feedstocks, F-2 (0.5 wt % N) and F-3 (0.75 wt % N), were obtained by blending F-1 with shale oil, F-4.

**FCC catalysts.** The commercial catalysts used in our tests were selected on the basis of catalytic activity, selectivity, and physical properties. Analytical data and properties of the commercial catalysts are shown in Table 2. The catalysts were selected from different manufacturers and differed significantly in their compositions and properties.

The data in Table 2 show that commercial catalysts K and L have high silica content, while catalysts N, O, and P have high alumina content.

Peak height measurements, chemical analysis, and microactivity test (MAT) data obtained with a low-nitrogen feedstock, show that catalysts L and P have higher contents of rare earth Y-zeolite (REY). Catalysts K, N, and O have lower zeolite contents and lower cracking activity.

Catalyst M is an octane-enhancing catalyst and contains ultrastable Y-zeolite (USY). These catalysts also have significant differences in surface area, pore volume, and bulk density.

**Testing method.** Steam-deactivated catalyst samples were tested with different feedstocks in a MAT unit. The steam deactivation was done with 100% steam at 760, 788, and 815° C., respectively, for 5 hr.

The MAT runs were done under the following conditions: 510° C. reaction temperature, 14.5 weight hourly space velocity (WHSV), and 3.5 catalyst/oil ratio. The cut point for gasoline was 232° C. and for LCO (light cycle oil), 355° C. DO (decanted oil) was the 355° C.$^+$ liquid fraction.

**Results and discussion.** MAT data obtained for six commercial FCC catalysts with feedstocks F-1, F-2, and F-3 are plotted in Figs. 2-7. Fig. 2 shows conversion and gasoline yields as a function of feed nitrogen for catalysts steam-deactivated at 788° C. for 5 hr.

The plots show a general decline in conversion and gasoline yield with increasing feed nitrogen content. Such a decline is due to increased poisoning of the catalysts by the nitrogen compounds in the feedstock.

The figure also shows that the most active among the catalysts tested are catalysts P and L. These two catalysts show a smaller decline in conversion and gasoline yields compared to the other catalysts.

Fig. 3 shows a general increase in LCO and DO yields with increasing feed nitrogen content. Catalysts P and L give the lowest LCO and DO yields.

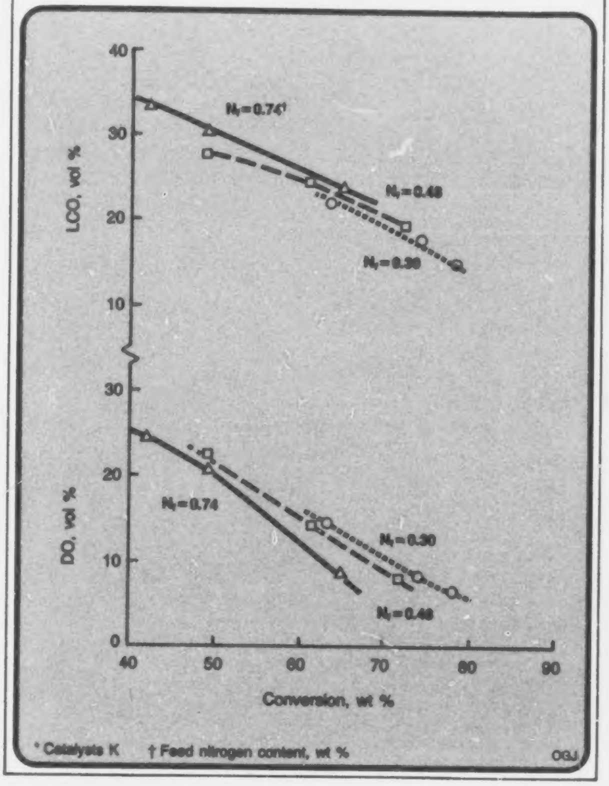
MAT data obtained with feedstock F-2 at constant coke make of 5.6 wt % are shown in Table 3. The data show that, under these conditions, catalyst P is the most active among the catalysts tested, giving the highest conversion and gasoline yield. However, the hydrogen yield obtained with catalyst P is also very high.

The high activity and gasoline selectivity of catalysts P and L are most likely due to the high content in rare-earth-exchanged Y zeolite, as indicated by the high x-ray diffraction (XRD) peak height values and high rare-earth content (Table 2). The differences in hydrogen selectivity between catalyst P and L (Table 3) are likely due to differences in the nonzeolitic components of the two catalysts. Such differences could also explain the higher activity of catalyst P vs. catalyst L, in spite of the higher peak height and rare earth content of the latter.

The effect of feed nitrogen content

Fig. 5

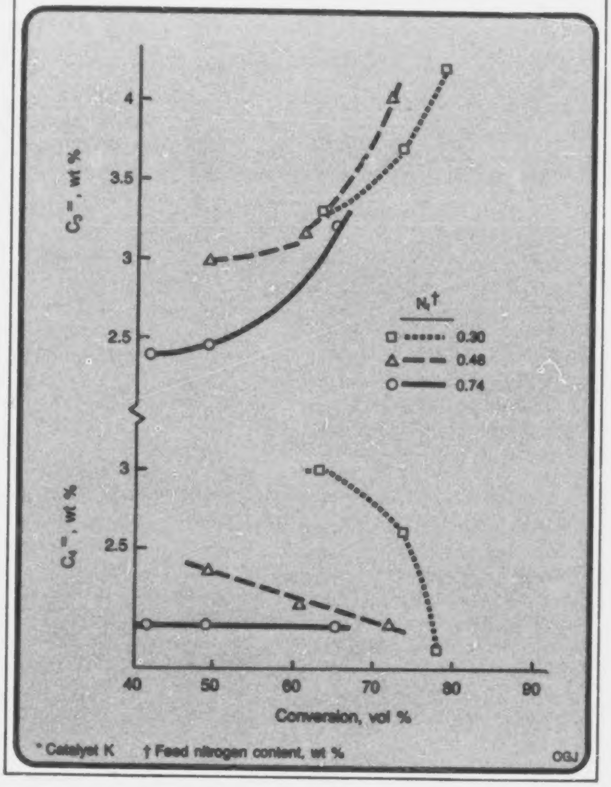
LCO and DO selectivities



* Catalysts K † Feed nitrogen content, wt %

Fig. 6

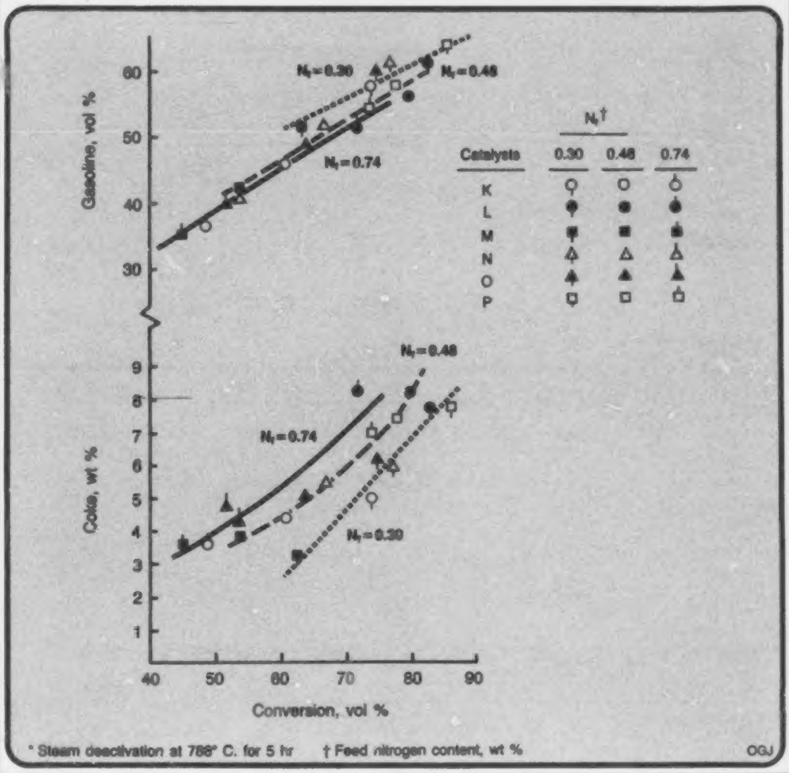
$C_3$ and $C_4$ olefin selectivities*



* Catalyst K † Feed nitrogen content, wt %

Fig. 7

## Tested catalysts, gasoline and coke selectivites*



* Steam deactivation at 788° C. for 5 hr † Feed nitrogen content, wt %

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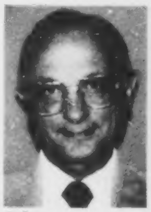
Table 2

## Composition and physical characteristics of commercial FCC catalysts

| Catalyst | K | L | M | N | O | P |
|---|---|---|---|---|---|---|
| **Chemical analyses** | | | | | | |
| $Al_2O_3$, wt % | 29.9 | 28.3 | 41.7 | 45.9 | 48.1 | 48.9 |
| $Na_2O$, wt % | 0.81 | 0.43 | 0.37 | 0.28 | 0.66 | 0.34 |
| $Re_2O_3$, wt % | 3.20 | 6.2 | 0.51 | 3.1 | 2.7 | 4.3 |
| **Physical properties*** | | | | | | |
| SA, sq m/g | 170 | 215 | 240 | 120 | 270 | 345 |
| ABD, g/cc | 0.90 | 0.80 | 0.74 | 0.77 | 0.72 | 0.86 |
| $N_2$-PV, cc/g | 0.18 | 0.19 | 0.22 | 0.24 | 0.38 | 0.37 |
| Hg-PV, cc/g | 0.62 | 0.52 | 0.67 | 0.71 | 0.96 | 0.72 |
| Pk. H., cps | 312 | 401 | 345 | 275 | 261 | 363 |

*SA = Surface area; ABD = Average bulk density; $N_2$-PV = Nitrogen pore volume; Hg-PV = Mercury pore volume; Pk. H. = Peak height in x-ray diffraction pattern, at $2\theta$ = 23.5°.

## The authors...



**Scherzer**

**McArthur**

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Before joining Unocal, Scherzer was with the Davison Chemical Division of W.R. Grace & Co. and with the Filtrol Co. He has more than 20 years' experience in zeolite chemistry and FCC catalysis, and he holds more than 40 U.S. and foreign patents. Scherzer is a graduate of the University of Bucharest and Johns Hopkins University.

Dennis P. McArthur is manager of process development at Unocal's science and technology division. Since joining Unocal in 1971, he has held positions of manager of refining research and of catalyst research. McArthur has a PhD in chemical engineering from Yale University.

on gasoline, coke, LCO, and DO selectivities, as a function of conversion, is illustrated in Figs. 4 and 5, using catalyst K as an example. The plots in Fig. 4 show that at constant conversion, an increase in feed-nitrogen content results in an increase in LCO and a decrease in DO yields.

The decrease in DO yield with higher feed nitrogen content at constant conversion illustrates an interesting selectivity effect caused by the nitrogen compounds in the feedstock. It suggests that a higher nitrogen content favors DO conversion.

The increase in DO conversion can be understood if one considers that the reaction severity—or catalyst activity—has to be increased when cracking a feed with higher nitrogen content in order to maintain constant conversion.

Correlations similar to those described for catalyst K have been found for other catalysts investigated. The effect of feed-nitrogen content on catalytic selectivity can be seen for catalysts N and O in Table 4.

The data show that at constant conversion (64 vol %), an increase in feed-nitrogen content results in a decrease in gasoline and DO yields and an increase in LCO, coke, and hydrogen yields. Also, the bigger the change in feed-nitrogen content, the more significant are the selectivity changes observed. Fig. 6 shows the effect of feed nitrogen content on $C_3$ and $C_4$ olefin selectivities as a function of conversion for catalyst K. The plots show that the $C_3$ and $C_4$ olefin yields are strongly affected by both conversion and feed nitrogen content results in lower $C_3$ and $C_4$ olefin yields.

Fig. 7 shows gasoline and coke yields as a function of conversion for the catalysts investigated, using feeds with different nitrogen content. The plots show that the relationships established for catalyst K apply to all the catalysts investigated.

At constant conversion, an increase in feed nitrogen results in a decrease in gasoline yield and an increase in coke make. In spite of the significant differences in composition and properties of the catalysts tested, at constant feed nitrogen content, the gasoline-vs.-conversion plot shows a linear relationship. The nitrogen content of the liquid products, as a function of conversion for different catalysts, is shown in Fig. 8. At constant feed-nitrogen content, the nitrogen content of the liquid products decreases with increasing conversion.

Furthermore, at constant conversion, an increase in feed-nitrogen content results in an increase of nitrogen content in the liquids products. Mass spectroscopic analysis has shown that most of the nitrogen compounds are in the DO and LCO fractions.

Nitrogen analysis of spent catalysts has shown that the amount of nitrogen on the catalyst is considerably smaller than in the corresponding liquid product. For example, catalyst K tested with feed F-1 gave, at 74 vol % conversion, a liquid product containing 1,100 ppm nitrogen, while the corresponding catalyst contained only 190 ppm nitrogen. At constant feed-nitrogen content, an increase in conversion results in an increase in nitrogen content of the catalyst.

Fig. 9 is a plot of percent nitrogen recovered in the liquid product vs. conversion for the catalysts investigated. Percent nitrogen recovered is defined as the ratio of percent nitrogen in liquid product and percent nitrogen in feed, times 100.

The plot shows a general decline in percent nitrogen recovered with increasing conversion, regardless of catalyst tested. All catalysts line up on the same curve, regardless of feed-nitrogen content. The lower concentration of nitrogen in the liquid product obtained with the more active catalysts, and the corresponding higher concentration of nitrogen on the spent catalysts, indicates stronger conversion of feedstock-nitrogen compounds into coke components.

**Conclusions.** The conclusions drawn from the data presented can be summarized as follows:

Table 3

## MAT data at constant coke make (5.6 wt %)*

| Catalyst | K | L | N | O | P |
|---|---|---|---|---|---|
| Conversion, vol % | 68 | 68 | 70 | 65 | 73 |
| Gasoline, ($C_5$-232° C.), vol % | 50.5 | 52 | 53 | 50 | 56 |
| LCO, vol % | 21 | 19.5 | 19.5 | 23.5 | 19.5 |
| $H_2$, scf/bbl | 87 | 62 | 85 | 102 | 158 |
| Steam-deactivation, °C. | 771 | 805 | 785 | 776 | 816 |

*For feed F-2 (0.48 wt % N)

Table 4

## Catalyst selectivity at constant conversion (64 vol %)*

| Catalyst | O | | N | |
|---|---|---|---|---|
| Steam-deactivation, °C. | 750 | 788 | 760 | 815 |
| Feedstock, (wt % nitrogen) | F-3 (0.74) | F-2 (0.48) | F-3 (0.74) | F-1 (0.30) |
| Conversion, vol % | 64 | | 64 | |
| Gasoline ($C_5-232$° C.), vol % | 48.6 | 49.0 | 46.8 | 52.2 |
| LCO, vol % | 25.7 | 24.3 | 24.5 | 22.7 |
| DO, vol % | 10.3 | 11.7 | 11.5 | 13.3 |
| Coke, wt % | 5.7 | 5.1 | 5.9 | 3.4 |
| $H_2$, scf/bbl | 113 | 101 | 94 | 77 |
| $C_1-C_3$, wt % | 7.84 | 7.11 | 8.33 | 7.01 |
| $C_3^=$, wt % | 2.92 | 3.30 | 2.95 | 3.46 |
| $C_4^=$, wt % | 2.40 | 2.87 | 2.12 | 2.63 |

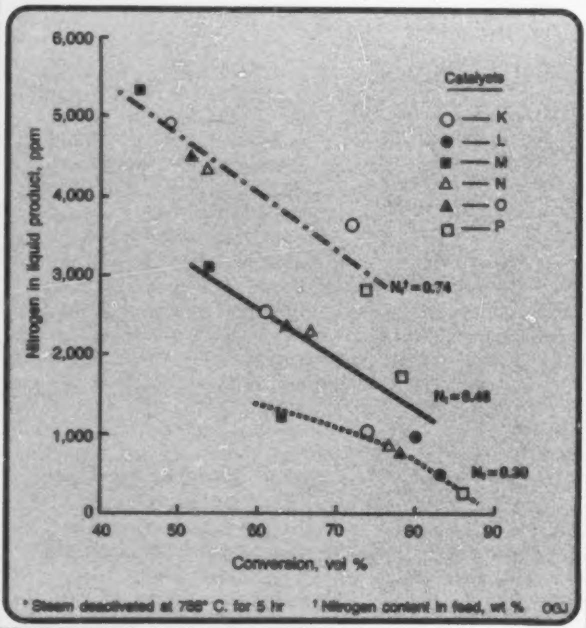
### Effect of feed nitrogen on yields at constant conversion (64 vol %)

| Change of: | Catalyst O | Catalyst N |
|---|---|---|
| Feed nitrogen, wt % | + 0.26 | + 0.44 |
| Gasoline yield, vol % | − 0.4 | − 5.2 |
| LCO yield, vol % | + 1.4 | + 1.8 |
| DO, vol % | − 1.4 | − 1.8 |
| Coke make, wt % | + 0.6 | + 2.5 |
| $H_2$, scf/bbl | +12 | +17 |
| $C_1$-$C_3$, wt % | + 0.73 | + 1.32 |
| $C_3^=$, wt % | − 3.38 | − 0.51 |
| $C_4^=$, wt % | − 0.47 | − 0.51 |

*Steam deactivated at different temperatures and using different feedstocks.

Fig. 8

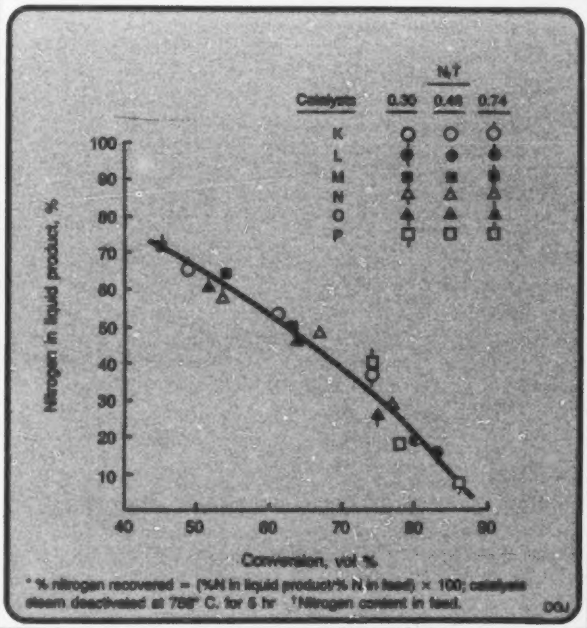
## Nitrogen content of liquid products*



* Steam deactivated at 788° C. for 5 hr † Nitrogen content in feed, wt % OGJ

Fig. 9

## Recovery of nitrogen in products*



* % nitrogen recovered = (%N in liquid product/% N in feed) × 100; catalysts steam deactivated at 788° C. for 5 hr † Nitrogen content in feed. OGJ

- At constant steam-deactivation temperature, an increase in feed-nitrogen content results in a decrease of conversion and gasoline yields and an increase in LCO and DO yields (Figs. 2 and 3).
- At constant conversion, an increase in feed-nitrogen content results in a decrease in gasoline and DO yields and an increase in LCO, coke, and hydrogen yields (Figs. 4, 5, and 7 and Table 4).
- At constant feed-nitrogen content, the nitrogen content of the liquid products decreases with increasing conversion (Fig. 8).
- The percent nitrogen recovered in the liquid products decreases with increasing conversion, regardless of feed nitrogen content (Fig. 9).
- Most of the nitrogen compounds in the liquid products are in the LCO and DO fractions.
- Catalysts P and L have the highest activity among the catalysts tested, regardless of steaming temperature of feed-nitrogen content (Fig. 2).
- Catalysts P and L gave the highest gasoline and coke yields, as well as the lowest LCO and DO yields.
- At constant coke make (5.6 wt %), catalyst P gave the highest conversion and gasoline yield.
- High zeolite content and matrix type play a role in enhancing the nitrogen resistance of FCC catalysts.

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# FCCU operating changes optimize octane catalyst use

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The use of octane-enhancing catalysts in a fluid catalytic cracking unit (FCCU) requires changes in the operation of the unit to derive maximum benefits from the octane catalyst.

In addition to the impressive octane gain achieved by the octane catalyst, the catalyst also affects the yield structure, the unit heat balance, and the product slate by reducing hydrogen transfer reactions.

Catalyst manufacturers have introduced new product lines based upon ultrastable Y type (USY) zeolites which can result in 2 to 3 research octane number (RON) gains over the more traditional rare earth exchanged Y type (REY) zeolites.

Here are some operating techniques for the FCCU and associated processes that will allow maximum benefits from octane catalyst use.

**USY/REY differences.** In order to understand the differences in performance between REY and USY catalysts, a short discussion on the formulation differences between the two is in order.

A USY zeolite is a hydrogen-exchanged form of the Y-type zeolite. Extensive washing and heat treatment is required to produce a USY catalyst.

Furthermore, compared to an REY catalyst, the USY zeolite has an inherently lower activity. To maintain reasonable activity, more zeolite is required in a USY catalyst to achieve the desired unit conversion. Typically, USY catalysts demonstrate 3-4 numbers lower activity compared to an REY catalyst.

The octane catalysts generally contain either a small amount or no rare earth. Rare earths are known to increase the rate of hydrogen-transfer reactions as well as cracking reactions, with relatively small effect on the ratio of the two rates.

USY zeolites typically have a silica-to-alumina mole ratio of 7.0 or higher, compared to 5.0 for REY catalysts.

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Based on a paper presented at the Ketjen Catalyst Technical Seminar, Banff, Alta., Aug. 13, 1986.

The higher silica-to-alumina ratio causes the distance between the reflecting planes to decrease (because Al has a larger ionic radius compared to Si) and is measured by X ray as a decrease in the unit cell size $A_0$.

USY catalysts equilibrate to a lower unit cell size in the unit compared to an REY catalyst. Cell size decreases due to dealumination, causing a decrease in site density.

But with increasing silica-to-alumina ratio, site strength increases due to reduction in Al-Al interaction. The ratio of cracking rate to hydrogen-transfer rate increases, causing a more olefinic, high-octane, gasoline stream. Pine, et al., reported that octane enhancement with USY zeolites is a function of unit cell size.[1]

**Operating effects.** Although USY catalysts generally contain more zeolite per pound of catalyst than REY catalysts, the zeolite is less active. Consequently, USY catalysts usually indicate lower equilibrium activity (almost 3-4 numbers) than REY catalysts at the same makeup rate, as indicated by microactivity (MAT) tests.

**Lower delta coke.** USY catalysts make less coke per pound of catalyst circulation or reduce delta coke compared to REY catalysts. Lower delta coke results in a lower regenerator temperature.

The lower regenerator temperature causes an increase in catalyst circulation rate to satisfy the heat demands in the reactor. The increased catalyst circulation and cat/oil ratio raises the conversion level.

So, although the USY catalysts have a lower microactivity, the unit conversion may still be maintained or perhaps will decrease slightly (far less than indicated by equilibrium activity). For those units that are circulation limited, other independent variables such as feed preheat may have to satisfy the heat demands of the reactor.

The endothermic heat of reaction is a measure of the energy required to crack the feed. It is very difficult to measure the heat of reaction accurately. Usually, it is estimated as the difference between the heat supplied to the reactor by the catalyst and the heat required for feed vaporization, losses, etc. in the reactor.

In spite of the inherent inaccuracy in measuring heat of reaction, it is generally observed that USY catalysts require a higher heat of reaction compared to REY catalysts. Typical values for REY catalysts are 120-140 BTU/lb compared to 140-180 BTU/lb for USY catalysts.

From MAT testing at various temperatures, it is possible to confirm that USY catalysts have a higher activation energy than REY catalysts. This higher activation energy with USY catalysts implies that the conversion gap between an REY and a USY catalyst can be reduced by an increase in reactor temperature. Although this route to increased unit conversion can be achieved without severe coke penalty, dry-gas make may increase beyond compressor capacity.

The USY catalysts have a lower hydrogen-transfer reaction rate compared to REY catalysts. Consequently, gasoline produced with USY catalysts is more olefinic, resulting in higher octane.

Since the hydrogen transfer reactions are exothermic, inhibition of these reactions with USY catalysts reduces the exothermic heat release in the reactor. This results in a higher cracking heat of reaction, as mentioned earlier.

**Yield structure changes.** The use of USY catalysts results in changes in yield structure. For the most part, these changes can be overcome by minor operational responses. An awareness of possible changes "a priori" will assist the refiner in deriving the maximum benefit with the USY catalysts.

USY catalysts normally increase the volume yield of dry gas. Furthermore, the hydrogen-to-methane ratio increases due to increased hydrogen yield, resulting in a lower molecular weight dry gas. Increased hydrogen yield is observed when the unit maintains the same conversion level (obtained with reactor temperature or catalyst-to-oil ratio) as with an REY catalyst.

If the unit operates at a lower conversion level with the USY catalyst, the hydrogen yield may remain unchanged; however, methane yield will decline, causing the hydrogen-to-methane ratio to increase, lowering the molecular weight.

Both of these factors, increased yield of dry gas and lower molecular weight, can cause surge problems in centrifugal compressors. Gas-flow meters will give erroneous readings. The heat capacity of the fuel gas will change, causing changes in burner operation.

**Operational response.** The increased yield of dry gas may exceed compressor capacity. A larger compressor or a backup compressor may be considered if other corrective actions are ineffective.

If the metals level on the catalyst, especially nickel, is sufficiently high (1,000 ppm or higher) antimony passivation could become cost effective.

To increase the molecular weight of the dry gas, vaporized propane could be recycled into the compressor suction.

Gas flow meters must be recalibrated for the reduction in the molecular weight. This is necessary to obtain an accurate material balance. Fuel gas burner settings must be reset to accommodate the lower-BTU gas.

**Increased olefinicity.** The USY catalysts inherently increase the olefinicity of the $C_3$'s and $C_4$'s. As discussed earlier, the major reason for the increased olefinicity is the reduction in hydrogen transfer activity of the USY catalysts.

The increased olefinicity can have the following effects:

- In a gas plant, an increase in compressor fouling may be observed, especially if diolefins are present. Also, propylene loss to fuel gas increases. Because relatively more propylene is produced (compared to REY catalysts), propylene rejection increases with $H_2S$.

If excessive fouling of the compressor is observed, increased naphtha wash may provide some relief. Alternately, inhibitor injection would also help to reduce fouling.

- In an alkylation unit, dryer fouling may increase for the same reason that the gas plant compressor fouls. Because the alky feed is more olefinic, the isobutane requirement increases. The increased olefinicity causes the alkylation reactor heat load to increase as more alkylate is produced. The higher heat load increases alkyl-

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ation reactor temperature causing octane loss and formation of undesirable heavy hydrocarbons.

Dryers should be watched closely and may have to be changed out more frequently to maintain fouling at low levels. An adequate supply of isobutane must be assured for uninterrupted operation to take full advantage of the increased olefin content. To facilitate excess heat removal, cooling water may be increased, or a recirculating pump could be added on the reactor heat exchanger.

- In a polymerization unit, the higher olefin content will necessitate an increased quench requirement. Increased heat removal downstream of the reactor will be necessary. Increased olefinicity in the feed will result in a higher gasoline yield per barrel of feed, increasing gasoline loading in the depropanizer, debutanizer.

A larger quench pump and increased cooling water on the heat exchanger may be considered for increased heat removal. The higher gasoline loading may require a larger reboiler on the poly gasoline stabilizer (debutanizer column). Retraying or repacking of this column may be required.

**Light cycle oil.** Another benefit of USY catalysts is the decrease in the specific gravity (increased API gravity) of the cycle oil (LCO) streams. Because these catalysts reduce hydrogen transfer, the cycle oils are hydrogen rich (paraffinic, naphthenic), and the lighter components such as gasoline and LPG are hydrogen lean (olefinic, aromatic). Consequently, the cycle oils have a lower specific gravity.

The lower specific gravity causes erroneous meter readings. Control valve settings may change. Meter factors are affected by viscosity as well, though generally light cycle oil temperatures are sufficiently high enough so that viscosity changes are small.

Because the light cycle oil is more paraffinic, its quality as a blending stock will generally improve with high cetane contribution and also stability. Light cycle oil is often used as flush oil in heavy cycle meters, clarified slurry meters, light cycle pumps, and heavy cycle pumps. Because the LCO specific gravity is lower and is more paraffinic, flush-oil requirements may decrease, especially in pump packings.

The heat-exchange capacity will change because of the lower weight per unit volume. The most positive effect of the USY catalysts is the impressive increase in cetane index. Cetane index increased from 29.5 to 33.0 when Keten OctaBoost-605 replaced an REY catalyst at a U.S. refinery.

The lower specific gravity of the LCO is desirable in most cases and provides added economic benefit. The refiner may welcome this benefit.

Flow meters should be recalibrated for the new gravity and viscosity. Cooler designs should be checked. Heat exchanger loading on LCO reboiler circuit and flow meters should be checked.

**Slurry oil.** Slurry oil specific gravity decreases for the same reasons as the LCO gravity. In this case, possible specification problems may arise for slurry oil used as carbon black oil or as needle coke feed, both of which require high specific gravity (or low API gravity −3.0 to 4.0-5.0 API).

We have not explored the sulfur content in the slurry oil with USY catalysts. An increase in sulfur is undesirable if the slurry oil is used in needle coke feed.

The lower specific gravity causes erroneous meter readings. Viscosity effects are more critical in slurry oil than in light cycle oil.

Heat exchange capacity will change and may cause problems in borderline cases.

Slurry-oil meters must be recalibrated for the new gravity and viscosity. Control valve settings must be checked.

If slurry oil is used as carbon black or needle coke feed, recycle could be increased to raise the specific gravity. Cut point changes (LCO end point) may also become necessary. Reactor temperature could be increased but this will also increase gas make.

**Coke make.** One of the most significant differences between USY and REY catalysts is the effect on heat balance and coke make. USY catalysts reduce coke make, as explained earlier. The reduction in coke make may have the following effects:

- On units in complete combustion, the $CO_2$-to-CO ratio is infinity. USY catalysts reduce the regenerator temperature on such units. Reductions from 1,350° F. to 1,330° F. have been observed. Accompanying this change is a reduction in steam yield from the flue gas boiler.
- On units in partial combustion, the $CO_2$-to-CO ratio is typically 6.0 to 8.0. USY catalysts reduce regenerator temperature. Adjustments such as CO combustion promotion may be made, which will reduce steam yield from the CO boiler.
- On units in conventional combustion, $CO_2$-to-CO ratios are close to 1.0-3.0. With the USY catalysts, the dense-bed temperature is lower compared to REY catalysts. This results in increased afterburn in the dilute phase. Also, steam yield from the CO boiler declines.

In order to return the unit to heat balance, several operational responses, some desirable, others undesirable, are possible.

The most desirable way to increase coke make and raise regenerator temperature for units in complete combustion is to add a resid slip stream into the feed. Coke precursors present in resid will raise regenerator temperature to return the unit to heat balance.

Feed preheat could also be raised to increase regenerator temperature.

Increasing recycle will also raise regenerator temperature. However, this approach is not as desirable as adding resid.

In some instances, torch oil has been used to raise regenerator temperature.

This is never desirable. Torch oil can damage catalyst activity by zeolite destruction.

Returning a unit in which torch oil is injected to normal activity level may require rapid replacement of a large portion of the catalyst inventory with new catalyst at a high cost.

Use of a CO combustion promoter can raise the regenerator temperature by increasing the $CO_2$-to-CO ratio for units in partial combustion. The loss in flue-gas boiler steam can be recovered by additional fuel gas.

**For units in conventional combustion.** CO-combustion promoter can increase burning in the dense bed, thereby raising the dense bed temperature.

This will also minimize incidents of afterburn. Air blower rate can also be lowered to control dense bed temperature.

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# Precious-metals supply adequate for catalysts

The availability of precious metals, platinum, palladium, and iridium, should be adequate for the forseeable future. But the effects of future new or expanded uses of these metals could make them less available.

That's the conclusion of A.H. Neal, commercial catalyst development coordinator for Exxon Research & Development Laboratories, Baton Rouge, La.

In a presentation before the International Precious Metals Institute, earlier this year, Neal presented the results of a study of the precious metals needs for the manufacture of catalysts primarily for catalytic reforming, isomerization, and hydrocracking.

"Platinum is an absolute must for modern refining as we know it, but the net requirement is so low, compared to normal production and demand, that there should always be enough for refining uses. In fact, it is so critical to refining, that I believe refiners could outbid other platinum users for the small amount which they must have," said Neal.

"With respect to palladium and iridium, there are reasonable alternatives for the catalysts utilizing these metals, so that in an absolute crisis, alternatives are available," he said.

The impact of platinum availability on refiners is important in light of the worldwide demand situation for platinum as seen by a major supplier.

"Western world demand for platinum increased by about 7% last year, but supply to the market grew by only 1%," according to Johnson Matthey Ltd., Toronto, in its publication, Platinum 1986.

**Isomerization catalysts.** Catalysts used in the various isomerization processes are generally two different types, according to Neal. They are either platinum on acidified alumina or platinum on a zeolite or molecular sieve support.

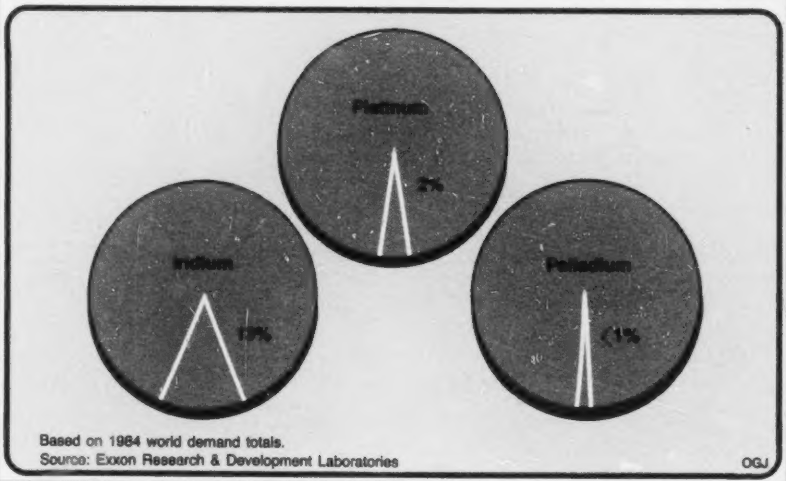
"In all cases, the platinum content of the catalyst is between 0.2 and 0.4%," said Neal. "At this time, there are about 70 paraffin isomerization units operating in the free world, totalling about 450,000 b/d capacity. There are about 2.1 million lb of isomerization catalyst in place, which is equivalent to about 89,000 troy oz of platinum.

"Based on an average catalyst life of about 4 to 5 years, the turnover of catalyst and platinum each year amounts to about 50,000 lb of catalyst and about 21,000 troy oz of platinum. When the catalyst in these units is deactivated or spent, most of the platinum is recovered and used to make new catalyst."

During the recovery of platinum from the spent catalyst, however, some platinum is lost in the manufac-

Fig. 1

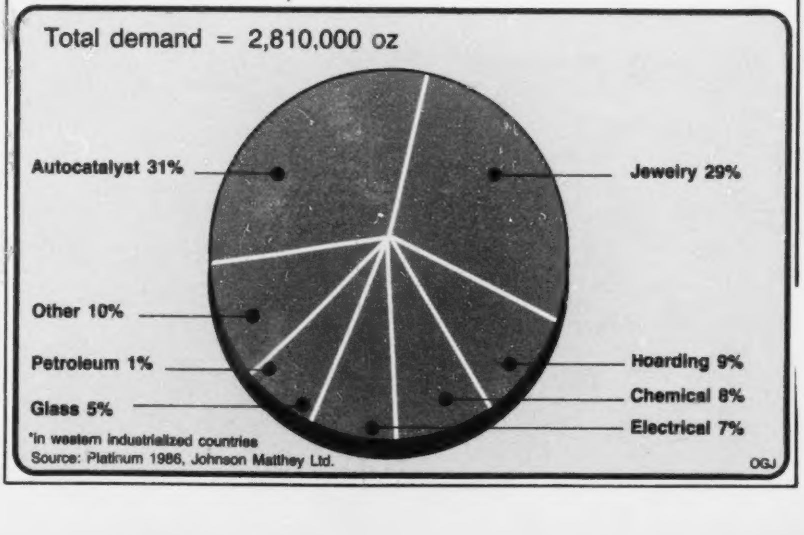
Refining precious metal needs vs. world demand*



Based on 1984 world demand totals.
Source: Exxon Research & Development Laboratories

Fig. 2

Platinum demand, 1985 *



*In western industrialized countries
Source: Platinum 1986, Johnson Matthey Ltd.

ture of new catalyst and lost to loading, unloading, and shipping of the catalyst.

"It is estimated that the net amount of platinum required to make up these losses is about 1,700 troy oz/year. Because of the construction and startup of several new units, to adjust to the lead phase out, however, initial catalyst charges will be required over the next 2 years which are estimated to require about 40,000 troy oz of additional platinum,"says Neal.

**Catalytic reforming.** There are about 25 to 35 different catalytic reforming catalysts available (see p. 39) and these all contain platinum on an alumina support. Many of these also contain promoter metals such as rhenium, iridium, and tin. The metal concentrations for these catalysts is in the range of 0.25 to 0.7 wt %.

"There are nearly 500 catalytic reformers in refineries in the free world," said Neal. "It is estimated that these units contain nearly 52 million lb of catalyst.

"Because of the great variation in the designs of the units, the types of catalysts, and the processing severities, the estimates for precious metal requirements must be considered rather imprecise. Using the best available data, however, it has been estimated that the total amount of platinum in these units is about 3 million troy oz.

"Because of the relatively few units employing Ir-containing catalysts, the corresponding iridium in place is only about 40,000 troy oz," says Neal. "It has been estimated that the annual turnover for Pt-containing catalysts is equivalent to about 500,000 troy oz/year."

Neal estimates the total net requirements for metals in these catalysts at 40,000 troy oz for platinum and about 3,000 troy oz for iridium.

**Hydrocracking.** Hydrocracking units used for processing heavy, contaminated feeds use precious metals catalysts. But only a small fraction of the units in place employ precious metals catalysts. These units use palladium-containing catalysts.

"It is estimated that the palladium content of the hydrocracking catalysts totals about 200-250,000 troy oz of palladium," says Neal. "Considering the average life of the catalysts, and the losses associated with reclaiming, it is estimated that the net palladium requirement is about 15-20,000 troy oz/year."

Refining processes such as lube processing, hydrocarbon solvent purification, and combustion promoters for fluid catalytic cracking operations also use a small amount of platinum in the catalysts used in these operations.

The amounts of platinum are difficult to measure, but it is estimated that about 10,000 troy oz of platinum/year are required, according to Neal. Fig. 1 shows today's total precious metal needs of today's refiners, compared to the 1984 worldwide demand for all uses for the three metals. Refining needs for platinum amount to about 2% of the total 1984 industry demand, palladium amounts to only 1% of total industry demand, but iridium needs represent about 13%, or about 23,000 troy oz.

**World platinum demand.** Johnson and Matthey Ltd. reported a 100,000 oz shortfall of platinum supplies during 1985. Demand in the western industrialized countries for platinum last year was 2,810,000 oz vs. 2,740,000 oz of supply.

Fig. 2 shows the distribution of platinum demand among the various users. In particular, note that refining accounts for about 1% of the demand.

The report also states that the supply of platinum to refiners should be adequate.

"The petroleum refining industry has lost most of its former importance as a high-volume outlet for new platinum, but more than 2-million oz are in service in refineries worldwide, and the metal still plays a critical part in the catalytic reforming process to produce high-octane fuels," says the report. "New demand may arise from refineries opening up in the third world, but possibly not sufficient to offset slimming down elsewhere.

"Metal surplus to requirements continued to be sold by refineries in Western Europe in 1985. Moreover, instead of intensive reforming there are alternative ways, using little or no platinum, of enhancing gasoline octane. While basic reforming will still be necessary, these possible new routes to high-octane unleaded fuel may inhibit the increase in demand for platinum that has been suggested by some commentators." ▪

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# Efficient carbon rejection upgrades Mexico's Maya crude oil

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Poor-quality crude oils and resids can be effectively upgraded by a chemically efficient carbon-rejection process followed by hydrotreating.

The effectiveness is demonstrated by utilizing the asphalt residual treating (ART) process to upgrade whole Maya crude oil from Mexico, in a 100,000-b/d refinery.

Maya was chosen because it represents most of the world's poor-quality crude oils and resids, and because the results of processing Maya will be similar for other poor-quality feedstocks. Here is a review of the upgrade process, along with investment and operating economics of the Maya upgrade.

For years, residues have been processed by either cooking for long periods of time, or by stuffing in hydrogen at high pressure with large amounts of catalyst. We've commonly called these processes "carbon-out" or "hydrogen-in."

Realistically, however, when talking poorer-quality feedstocks, these processes should be called "carbon-out followed by hydrogen-in" or "hydrogen-in followed by carbon-out." For example, most coker products require hydrotreating and most hydrotreated resids would require fractionation (carbon-out) before being processed in a conversion unit.

Because the primary objective of upgrading residues is to maximize the production of gasoline and distillate, it is usually necessary to improve the hydrogen content of residue-derived feeds prior to processing in downstream conversion units. The obstacles to realizing this objective are: heavy metals, nitrogen compounds, sulfur compounds, and coke formers contained in the feed because of their

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Based on a paper presented at the National Petroleum Refiners Association annual meeting, Los Angeles, Mar. 23-25, 1986.

Fig. 1

Whole-crude ART refinery

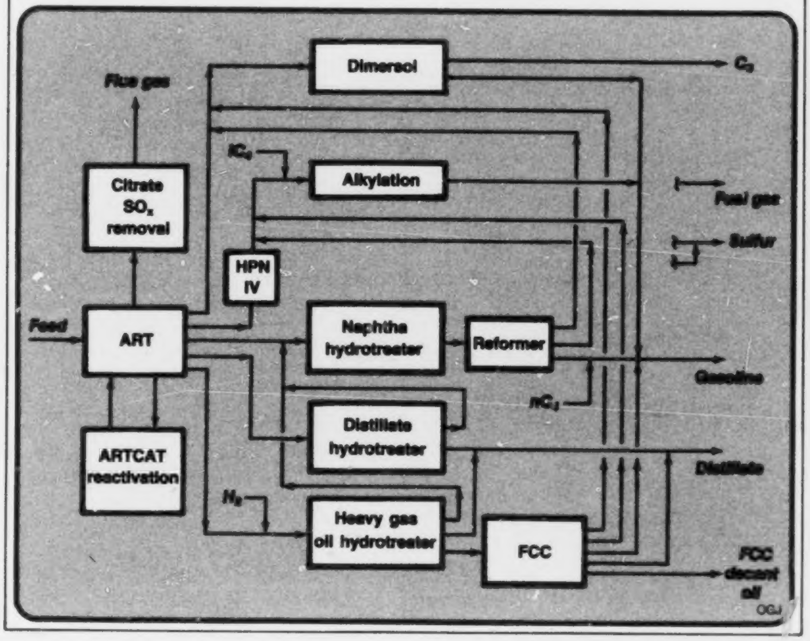
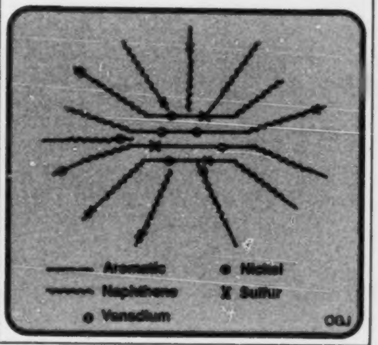


Fig. 2

Asphaltene structure



effects on the conversion catalysts and/or the yields obtained. For example, hydrotreating of poor-quality resids does not accomplish the required contaminant removal, so some form of carbon injection is also required.

Here we have the crux of the problem—carbon-rejection processes used to date are just not chemically efficient. They degrade usable portions of the oil to coke and produce degraded products.

**Residue comparison.** For illustration, Table 1 defines the quality of various atmospheric residues which have been considered for direct hydrotreating over the years. Progressing from Kuwait through Venezuelan crudes in Table 1, it is obvious that as the asphaltenes increase, all of the contaminant levels become excessively high.

As can be seen, even if the operation were lucky enough to achieve 90% metals removal via hydrotreating, the poor-quality resid feeds still make poor-quality products. They cannot be directly processed in downstream conversion facilities such as heavy oil fluid catalytic cracking units (FCCUs) or hydro-crackers without excessive catalyst costs.

For instance, assuming that Maya resid could be hydrotreated to high metals removal, the product would still have at least 40 ppm of metals and 2-3% asphaltenes—not a good feed to a conversion unit. The data show that beyond the quality of Heavy Arabian atmospheric tower bottoms (ATB), it is time to stop stuffing hydrogen into the back end of the barrel. An efficient carbon-rejection process followed by optimum product hydrotreating is the answer.

**Carbon-out, hydrogen-in.** Fig. 2 shows a well-known picture of the so-called asphaltene structure that has been used by technologists all over the world. We don't know who originally conceived this representation, but surely the scientist caught the attention of those involved in residue upgrading.

The technical world has been trying for years to find some simple and efficient means of converting these molecules without significant degradation of the products. The carbon rejection processes we've been using so far have been simple, inefficient, brute-force approaches.

For example, the carbon residue content of the residuum has been commonly used to define its "coke-ability." It has been shown that delayed coking nets 1.5 to 1.7 times the Conradson carbon residue (CCR) as coke yield, and fluidized cokers yield 1.1 to 1.3 times the CCR as coke yield.

Realizing that the carbon residue includes the asphaltenes, as measured by $C_7$ insoluables, it's obvious that we've not only coked the asphaltenes, but also lost some of the crude oil's potential gasoline by coking a portion of the resin fraction of the oil. The coking factor of the ART process is 0.8 to 1.0 times the CCR, because only the asphaltenes are reacted upon. The resin fraction goes where it should—to primary fuels, not coke.

The ART process simply applies modern design techniques and catalytic thinking to residue chemistry. Where cokers require high contact time in a pressure-cooker environment, the ART process selectively vaporizes the good oils from the asphaltenes and then reacts and converts the asphaltenes in a matter of seconds. Fifteen years ago, our design techniques were so Spartan that this concept would have only been a laboratory success.

Table 1

## Residues considered for direct hydrotreating

| Crude | Kuwait | Arab.hvy. | Maya | Lloydminster | Orinoco |
|---|---|---|---|---|---|
| | ATB | ATB | ATB | ATB | 400° F. + |
| Gravity, °API | 17.0 | 12.7 | 8.5 | 9.0 | 9.0 |
| Sulfur, wt % | 3.9 | 4.4 | 4.7 | 4.7 | 3.5 |
| Nitrogen, wt % | 0.21 | 0.28 | 0.54 | 0.43 | 0.60 |
| $C_7$ insolubles, wt % | 4.0 | 11.0 | 14.5 | 12.0 | 12.0 |
| CCR, wt % | 8.5 | 13.6 | 17.2 | 15.0 | 17.0 |
| Ni + V, ppm wt | 70 | 120 | 480 | 210 | 550 |
| Viscosity, SUS at 210° F. | 200 | 420 | 2250 | 3000 | 3800 |
| **650° F. + product** | | | | | |
| Sulfur, wt % | 0.3-0.4 | 0.3-0.4 | 0.3-0.4 | 0.3-0.4 | 0.3-0.4 |
| Nitrogen, wt % | 0.1 | 0.15 | 0.15-0.2 | 0.2 | 0.25-0.3 |
| $C_7$ insolubles, wt % | 1-2 | 2-3 | 3-4 | 1-2 | 3-4 |
| CCR, wt % | 2-3 | 4-5 | 5-6 | 4-5 | 5-6 |
| Ni + V, ppm wt | 5-10 | 10-15 | 70-100 | 30-40 | 100 + |

Table 2

## Maya crude properties

| | |
|---|---|
| Gravity, °API | 23.5 |
| Sulfur, wt % | 3.0 |
| $C_5$ insolubles, wt % | 12.3 |
| $C_7$ insolubles, wt % | 11.1 |
| Nitrogen, total, ppm | 3000 |
| Nitrogen, basic, ppm | 840 |
| Nickel, ppm | 24 |
| Vanadium, ppm | 240 |
| Sodium, ppm | 8 |
| Hydrogen, wt % | 11.96 |
| Carbon, wt % | 84.86 |
| C/H ratio | 7.10 |
| Ramsbottom carbon, wt % | 9.7 |

Table 3

## Comparison of whole Maya crude with ART-produced crude

| | Crude | $C_5$ + ART-crude |
|---|---|---|
| Gravity, °API | 23.5 | 31.5 |
| Volume % | 100.0 | 90.5 |
| Sulfur, wt % | 3.0 | 2.1 |
| $C_5$ insolubles, wt % | 12.3 | 1.1 |
| $C_7$ insolubles, wt % | 11.1 | 0.7 |
| Nitrogen, total, ppm | 3000 | 660 |
| Nickel, ppm | 24 | 1.4 |
| Vanadium, ppm | 240 | 7.7 |
| Sodium, ppm | 8 | 0.2 |
| Hydrogen, wt % | 11.96 | 12.65 |
| Carbon, wt % | 84.86 | 85.19 |
| C/H ratio | 7.10 | 6.73 |
| Viscosity of 650° F. + reduced crude, cSt at 210° F. | 211 | 12 |
| **Yields, vol %** | | |
| $C_5$-430°F. | 20.0 | 26.5 |
| 430-650° F. | 21.0 | 29.1 |
| 650° F. + | 58.1 | 34.9 |

Table 4

## Hydrotreating of ART naphtha*

| **Operating conditions** | | |
|---|---|---|
| Catalyst | | Shell 424 |
| Total pressure, psig | | 600 |
| LHSV, $hr^{-1}$ | | 4.0 |
| $H_2$ rate, scf/bbl | | 2500 |
| Temperature, °F. | | 625 |
| $H_2$ consumption, scf/bbl | | 250 |
| | **Feed** | **Product** |
| Gravity, °API | 51.2 | 53.1 |
| Hydrogen, wt % | 14.2 | 14.7 |
| Sulfur, ppm | 5300 | <0.5 |
| Nitrogen, ppm | 31 | <0.5 |
| Compound type, LV% | | |
| Saturates | 73.8 | |
| Paraffins | | 62.7 |
| Olefins | 11.6 | — |
| Naphthenes | | 24.9 |
| Aromatics | 14.6 | 12.4 |
| Bromine No. | 21.3 | 0 |
| MAV† | 15.4 | 0 |

*Full-range naphtha. †Maleic anhydride value.

**Maya refinery.** To show the effectiveness of the ART approach to Maya upgrading, the concept is applied to a 100,000-b/d refinery. The refinery is operated to minimize fuel oil. Hydrotreating of the ART products obtained is discussed in detail along with a comparison to direct hydrotreating of Maya resid because of the dramatic effect on economics.

Table 2 details the quality of the Maya crude processed in the ART unit. For continuity of the information relative to Maya crude, Table 3 contains the quality of the Maya crude and the $C_5$ + ART-crude—the blended crude which could be produced if that were the objective. Table 3 also compares the ART yields to crude yields from virgin Maya to illustrate the incremental changes due to the asphaltene conversion.

**Hydrotreating of products.** Proper hydrotreating of any fraction, whether of virgin or process origin, is necessary to ensure good refining economics. Anyone can design conservative hydrotreaters. But that won't maximize profits.

The key is to achieve the maximum from the catalyst and minimize the investment and operating costs. This was an integral part of the thinking behind the hydrotreating of the ART products.

In today's refineries, Shell catalysts are generally accepted to represent up-to-date technology. Thus, Engelhard and M.W. Kellogg, the licensor of the ART process, entered into a cooperative association with Shell Chemical to hydrogenate the products from the ART processing of full Maya crude. The work was done at Shell Development Co. near Houston. The following discusses the results of this work.

**Naththa hydrotreating.** The ART naphtha contains products of asphaltene conversion reactions. Table 4 shows that naphtha product from ART processing of Maya crude was hydrotreated to reformer feed quality using a nickel-molybdemum (NiMo) catalyst, Shell 424. The product had a naphthenes + 2K aromatics (N + 2A) content of 49, compared to 40-45 for virgin Maya naphtha of the same boiling range.

The conditions required were 4 liquid hourly space velocity (LHSV) with 600 psig total pressure, with an expected cycle life greater than a year. Hydrogen consumption was 250 scf/bbl.

**Distillate hydrotreating.** The distillate hydrotreating data are shown in Table 5. Operating conditions of 450 psig and 2.0 LHSV were used to treat the light gas oil (LGO) with Shell-424 catalyst. The Bromine number of the feed was 9, indicating about 4-5% olefins from the asphaltene conversion.

The mild treating saturated these olefins and produced a good-quality diesel fuel. The product has a 51 cetane index and 0.2 wt % sulfur. The catalyst cycle life would be at least a year for hydrotreating this distillate at the test conditions. Hydrogen consumption was 400 scf/bbl.

**Heavy gas oil hydrogenation.** This is the ART product that causes the most concern. Because the ART process does expose the feed to relatively

Table 5

## Hydrotreating of Art light gas oil

| **Operating Conditions** | |
|---|---|
| Catalyst | Shell 424 |
| Total pressure, psig | 450 |
| LHSV, $hr^{-1}$ | 2.0 |
| $H_2$ rate, scf/bbl | 1000 |
| Temperature, °F. | 625 |
| $H_2$ consumption, scf/bbl | 400 |

| | **Feed** | **Product** |
|---|---|---|
| Gravity, °API | 32.3 | 35.8 |
| Carbon, wt % | 85.40 | 86.56 |
| Hydrogen, wt % | 12.61 | 13.20 |
| Sulfur, wt % | 1.87 | 0.20 |
| Nitrogen, wt % | 0.039 | 0.010 |
| Total aromatics, wt % | 16.6 | 14.1 |
| Bromine No. | 9.3 | 1 |
| Cetane index | 50.0 | 51 |

high temperatures, the tendency is to think that the heavy gas oil (HGO) will be of similar quality to that produced from cokers.

If this were so, the hydrogen consumed in hydrotreating the ART HGO would be high, but it isn't. As can be seen in Table 6, the hydrogen consumption for treating the ART HGO to a 0.275 wt % sulfur product is 700 scf/bbl. Treating virgin Maya vacuum gas oil (VGO) at the same conditions would consume about 550-600 scf/bbl, while treating a Maya coker distillate would require well in excess of 1,000 scf/bbl.

Whereas the consumption with the ART product is somewhat higher than virgin VGO, due to the products of asphaltene conversion, it is nowhere near the hydrogen needed to treat products from the high-contact-time coking processes.

Because of the selective vaporization in the ART unit, the virgin VGO quality is virtually unaffected, and additional hydrogen beyond that required for contaminant removal is needed only to upgrade the incremental distillate produced by asphaltene conversion.

Also shown in Table 6 are the operating conditions: 1.5 LHSV, 1,200 psig total pressure, and 2,500 scf/bbl $H_2$ circulation; and the feed/product quality for hydrotreating the ART HGO using Shell's patented stacked bed catalyst stystem. The hydrotreating study ran for 37 days in the pilot plant with no change in catalyst stability.

Based on these data, the expected commercial cycle life for hydrotreating HGO is greater than 1 year. As shown by the product data in Table 6, the resultant liquid can be fed directly to an FCC unit. The metals and asphaltenes are gone and the nitrogen reduced to at least acceptable levels.

A comparison with direct resid hydrotreating is interesting at this point.

Table 6

## Heavy gas-oil hydrotreating

| **Operating conditions** | |
|---|---|
| Catalyst | Shell stacked bed catalysts |
| Total pressure, psig | 1200 |
| $H_2$ partial pressure at reactor outlet, psia (min) | 1000 |
| LHSV, $hr^{-1}$ | 1.5 |
| $H_2$ rate, scf/bbl at reactor inlet (min) | 2500 |
| Temperature, °F. | 700 |
| $H_2$ consumption, scf/bbl | 700 |

| | **Feed** | **Product** |
|---|---|---|
| Gravity, °API | 16.2 | 25.0 |
| Carbon, wt % | 85.21 | 87.40 |
| Hydrogen, wt % | 11.21 | 12.24 |
| Sulfur, wt % | 3.17 | 0.275 |
| Nitrogen, wt % | 0.245 | 0.140 |
| Metals, ppm, wt | 20.2 | 0 |
| $C_7$ insolubles | 0.2 | <0.02 |
| UV aromatics, wt % | 27.2 | 16.8 |
| Distillation, °F., vol % (D-1160) | | |
| IBP | 660 | 353 |
| 10 | 723 | 659 |
| 50 | 858 | 814 |
| 90 | 1060 | 1059 |
| EP | 1151 | |

To process Maya atmospheric resid in a fixed-bed system, such as discussed previously in Table 1, would require pressures of 2,000-2,500 psig, and volumetric space velocities of 0.1-0.2.

The ART heavy gas oil hydrotreater requires 1,200 psig and 1.5 LHSV—about 50% of the operating pressure, 10% of the catalyst requirement, and 40-50% of the hydrogen needed for treating Maya atmospheric resid. Hydrotreated ART product has no metals and undetectable asphaltenes and can be fed directly to an FCC unit.

As noted previously, hydrotreated products from direct processing of Maya resid would still contain a poor-quality residue and cannot be fed directly to a conversion unit without "carbon-out" via fractionation.

Because production of good-quality distillates is a major aim of some refiners, the ART process HGO was also treated in a mild hydrocracking mode, again using the Shell stacked bed catalyst system. Test conditions of 1,500 psig total pressure, 1.0 LHSV, and 3,500 scf/bbl gas rate were chosen for the mild hydrocracking tests because they represent the upper end of conventional gas-oil hydrotreater design conditions.

Table 7 presents the feed and product quality data for obtaining 25 wt % conversion of the ART process HGO at the test conditions. As evidenced, the 650° F. + liquid product has been further improved with nitrogen reduced to less than 500 ppm and zero metals and asphaltenes—a good FCC feed.

Table 7

## Mild hydrocracking of ART HGO

| **Operating conditions** | |
|---|---|
| Catalyst | Shell stacked bed catalysts |
| Total pressure, psig | 1500 |
| $H_2$ partial pressure at reactor outlet, psia (min) | 1200 |
| LHSV, $hr^{-1}$ | 1.0 |
| $H_2$ rate, scf/bbl at reactor inlet (min) | 3500 |
| Temperature, °F. | 760 |
| $H_2$ consumption, scf/bbl | 1000 |
| Conversion, wt % | 25 |

| | **Feed** | **Product** |
|---|---|---|
| Gravity, °API | 16.2 | 28.5 |
| Carbon, wt % | 85.21 | 87.24 |
| Hydrogen, wt % | 11.21 | 12.60 |
| Sulfur, wt % | 3.17 | 0.021 |
| Nitrogen, wt % | 0.245 | 0.045 |
| Metals, ppm, wt | 20.2 | 0 |
| $C_7$ insolubles | 0.2 | <.01 |
| UV aromatics, wt % total | 27.2 | 14.6 |
| Distillation, °F., vol % (D-1160) | | |
| IBP | 660 | 400 |
| 10 | 723 | 581 |
| 50 | 858 | 767 |
| 90 | 1060 | 1000 |
| EP | 1150 | 1065 |

Table 8

## Minimum fuel oil refining scheme*

| **Feed** | |
|---|---|
| Maya crude, b/sd | 100,000 |
| i-butane, b/sd | 1,715 |
| n-butane, b/sd | 5,600 |
| Hydrogen, MMscfd | 32.6 |
| Total feed, b/sd | 107,315 |
| **Products** | |
| $C_3$ LPG, b/sd | 2,355 |
| $C_4$, b/sd | — |
| Gasoline (regular unleaded, 11 Rvp, b/sd | 52,394 |
| Distillate, b/sd | 45,441 |
| FCC decant oil, b/sd | 2,793 |
| Fuel gas (FOE),† b/sd | 5,771 |
| Total products, b/sd | 108,754 |
| Sulfur, long tons/day | 415 |

*100,000 b/d whole Maya crude
†Fuel oil equivalent

**Minimum fuel oil.** Fig. 1 presents a minimum fuel oil/maximum transportation fuel refining scheme whose basis is full Maya crude ART processing. The scheme includes hydrotreating of the ART HGO product to FCC feed, but the gasoline/distillate ratio could be altered somewhat by using mild or full hydrocracking of ART HGO if that were the objective.

Table 8 presents the volumetric balance for this scheme. The yield of liquid products is 101.3%, the gasoline plus distillate or transportation fuels yield is 91.2%, and there is only a small amount of FCC slurry oil.

In fact, when compared on a grassroots basis to other published Maya processing schemes using traditional "carbon-out" processing, the transportation fuels yield is 8-14 vol % greater for the ART scheme. Further, a severe hydrotreating route with the same objective would also produce a significant amount of a high-metals fuel oil because of conversion restraints on the hydrotreater itself, and downstream conversion limitations.

The estimated investment for the 100,000 b/sd ART unit on a Gulf Coast basis, charging whole Maya crude, is $120-130 million, or $1,200-1,300/b/sd of capacity. This includes SOx abatement facilities (in this case the citrate process).

The estimated operating cost for processing Maya crude in the ART unit (including citrate process operating cost) is $1.00-$1.10/bbl of crude. This includes steam credit, sulfur byproduct credit, and the cost of the Artcat contact material using Artcat reactivation. This is less operating cost than the operation of a crude and vacuum unit to distill the same crude.

The estimated investments for the naphtha, light gas oil, and HGO hydrotreaters would vary considerably depending on the degree of conservatism and design philosophy used in the plant design. Generally, however, the range is as low as $700-800 b/sd for naphtha treating to as high as $1,500 for mild hydrocracking. Operating costs for the hydrotreaters would be typical for units operating in a modern refinery today.

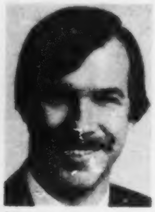
The discussions to this point have described the benefits of ART processing and hydrotreating products from the poorer types of crudes. Observation of the hydrotreating data allows one to conclude that there are many existing hydrotreaters in refineries today which can readily be used to hydrotreat the ART products.

Also, if the refinery happens to have two FCC units, there is some good news. Engelhard has developed a proprietary technology which can significantly increase the capacity of an existing reactor-regenerator structure at a fraction of the cost of a new structure. For example, if the FCC units are near equal in capacity, one can be converted to an ART unit with twice the original coke burning capacity, and the other can be revamped to process twice its original capacity allowing the VGO plus ART HGO to be processed for less cost than a grass roots ART unit.

The technology also allows the refiner with only one FCC to inexpensively increase unit capacity or to convert it into a heavy oil FCC with increased capacity. ▪

## The authors...

**Suchanek**


**Moore**

Arthur J. Suchanek is technology licensing manager of the specialty chemicals division of Engelhard Corp. He joined Engelhard in mid-1985 after 22 years with the Gulf companies. Suchanek's background includes all aspects of refining technology, but specialization in bottom-of-the-barrel upgrading and hydroprocessing.

He is a chemical engineering graduate of the University of Pittsburgh, and he served on the 1984 question and answer panel for the National Petroleum Refiners Association Q & A session on refining technology.

Suchanek has also authored papers on waste lube processing, the Gulf residue HDS process, naphtha isomerization, and chemically efficient refining operations.

A.S. Moore is an engineer with the specialty chemicals division of Engelhard Corp. He joined Engelhard's refining technology department in 1983, after service with UOP Inc. as a technical services engineer. Moore is a graduate of the University of Texas and is a member of AIChE.

# Octane catalyst

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To meet additional octane requirements prompted by lead-phasedown rules, Coastal Eagle Point Oil Co. chose an octane-enhancing catalyst for its Westville, N.J., refinery. But octane enhancement was not the only benefit needed from the catalyst.

Coastal also had to increase the amount of resid charged to the fluid catalytic cracker (FCC) because of the nature of the crude oils processed in the refinery, and because of the operating nature of the crude and vacuum units. The combination of octane enhancement and increased resid-charging capability was necessary to achieve acceptable economics for the overall operation.

The goal of improving gasoline octane while charging poor-quality feedstocks was achieved by switching to an ultrastable Y (USY) type catalyst, Filtrol ROC-1DY.

**Background.** Because of its key position in most refineries, the FCC unit must have the flexibility to process a wide variety of feeds. The operation of the cat cracker must also be adjusted and maintained at optimum conditions for maximum profitability.

Table 1

### Resid feed quantity boosted

| Feed property | Base operation | Current operation |
|---|---|---|
| Catalyst | REY | ROC-1DY |
| FCCU charge rate | Base | Base + 15% |
| Vacuum resid, vol % | 13-19 | 20-27 |
| Gravity, °API | 30 | 30 |
| UOP K | 12.05 | 12.0 |
| Molecular weight | 330 | 370 |
| Nickel, wt ppm | 3 | 5 |
| Vanadium, wt ppm | 0.5 | 0.5 |

# boosts octane, resid-charging capability

Fig. 1

Gas and coke selectivities

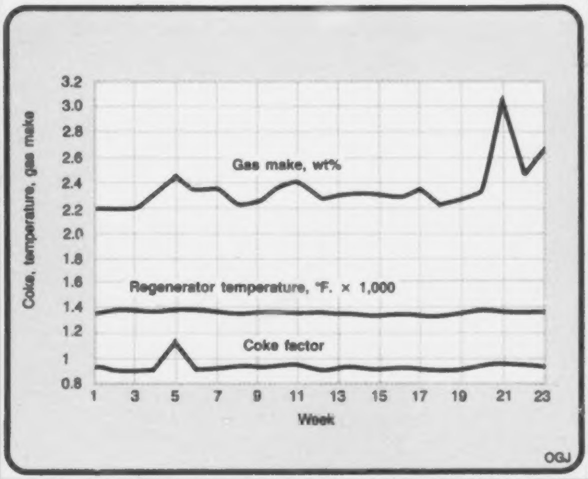
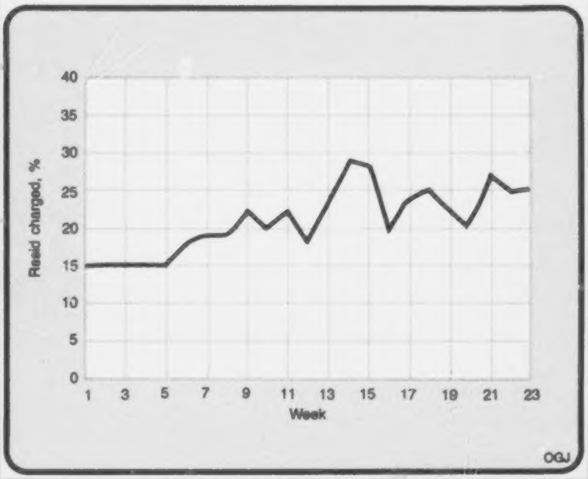


Fig. 2

Resid charge increased



Some older cat crackers can be mechanically revamped to enable processing a wider range of feedstocks.

For example, upgrading regenerator and reactor internals, and the addition of heat-removal equipment, will allow for adding significant quantities of residual feeds to FCC combined feed. However, in many cases the use of the proper catalyst system, combined with appropriate unit operation, will also provide the refiner with a wider selection of feedstocks for the FCCU.

When faced with the economic reality of having to process heavier and poorer-quality feeds with a tighter capital budget, both refiners and catalyst manufacturers need to respond with innovative techniques to improve profitability. Generally, octane-improvement options are constrained by particular unit design and operating parameters. The most important parameters are:

- Octane enhancing catalysts
- Operating severity
- FCC gasoline end point
- Feedstock selection

The latter three criteria are routinely optimized by refineries in their quest to maintain profitability. Use of new catalysts may well be the remaining major step toward improving a given FCC's profitability without major capital expenditures.

**Ultrastable zeolites.** It had long been theorized that ultrastable Y zeolites (USY) could enhance both gasoline research and motor octane levels without a significant negative effect on gasoline selectivity. Using a series of laboratory-synthesized FCC catalysts, Pine, et. al., of Exxon demonstrated the effect of USY unit cell size on catalytic octane performance and activity. As the unit cell size of steam-deactivated, USY-containing catalysts decreased, there was a steady and significant increase in both research and motor octane numbers, accompanied by a decreased microactivity test (MAT) activity and a strong tendency to make light $C_2-$ gas.

Also of considerable importance has been the USY's positive impact on coke selectivity.

Filtrol's research concentrated on the development of a zeolite system, taking advantage of the attributes of the conventional USY, while controlling the light gas production and maintaining acceptable activity levels. The result of this research effort was the development of dealuminated Y (DY) zeolite. Filtrol's dealuminated Y catalysts retain all the benefits of regular USY, while maintaining better activity and producing less light gas. In addition, Filtrol combines USY technology with a cost-effective matrix in its catalysts for upgrading heavy gas oils and resids.

The effects of feed contaminants, particularly metals, has been well documented. For the most part, metals are deposited quantitatively on the catalyst. These metals tend to nonselectively catalyze undesirable dehydrogenation reactions, while also causing a loss of surface areas and zeolite activity. For units processing large quantities of resid, containing high levels of nickel and vanadium, it is critical that a catalyst tolerate significant metals loading while continuing

Fig. 3

Gasoline octane increased

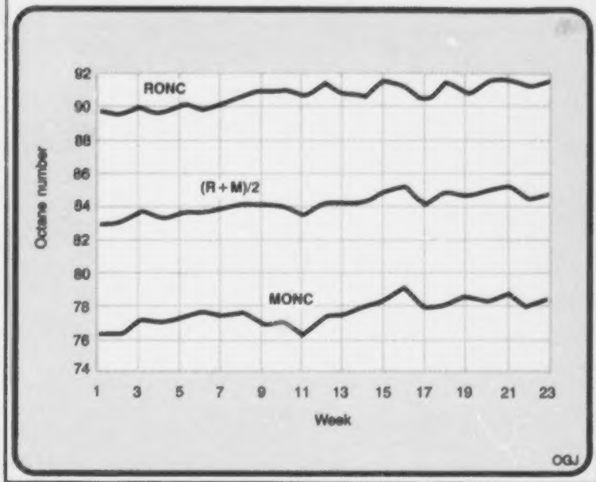


Fig. 4

Catalyst handles increased metals

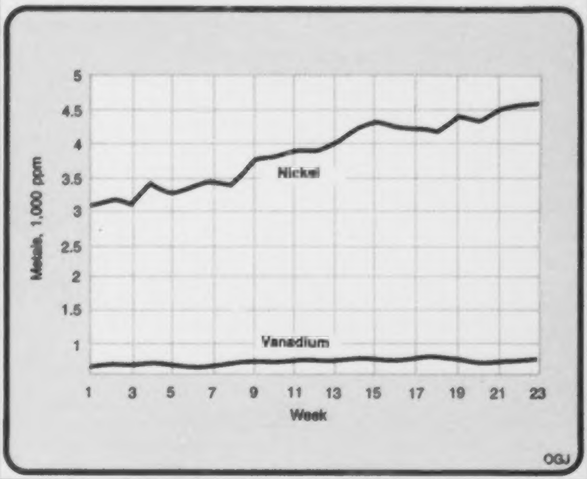


Table 2

## Feed and yields compared

| | Base operation | LCO mode | Gasoline mode |
|---|---|---|---|
| Charge rate | Base | Base + 15% | Base + 15% |
| Vacuum resid, vol % | 13-19 | 20-27 | 20-27 |
| Combined feed ratio | 1.10 | 1.20 | 1.12 |
| Riser outlet temp, °F. | 955 | 945 | 965 |
| Catalyst type | REY | ROC-1DY | ROC-1DY |
| Catalyst activity, MAT | 68 | 63 | 64 |
| **Yields** | | | |
| $C_2$ and lighter, wt % | 2.40 | 2.22 | 2.29 |
| $C_3$ + $C_4$, vol % | 20.9 | 17.6 | 18.8 |
| $C_5$ + gasoline, vol % | *60.3 | †48.8 | §59.8 |
| Light cycle oil, vol % | 17.0 | 29.8 | 22.5 |
| Decant oil, vol % | 10.3 | 11.0 | 10.6 |
| Coke, wt % | 4.7 | 3.6 | 4.1 |
| Gasoline RONC | 89.6 | 91.8 | 92.2 |
| MONC | 76.4 | 78.4 | 78.8 |
| (R + M)/2 | 83 | 85.1 | 85.5 |
| Ni + V on catalyst, wt ppm | 4,050 | 5,010 | 5,260 |

*430° F. ASTM end point
†350° F. ASTM end point
§430° F. ASTM end point
¶625° F. ASTM end point

to provide good performance.

**Coastal's application.** Coastal's Eagle Point refinery has improved FCC octanes without yield penalties while charging poor-quality feedstocks to the unit. This was accomplished primarily by switching to Filtrol ROC-1DY. This catalyst combines octane-enhancing dealuminated zeolites with an active matrix to provide octane improvements together with the flexibility to process heavily contaminated poorer-quality feedstocks.

Coastal Eagle Point primarily processes heavy paraffinic crudes from Indonesia and China. While such crudes generate typically excellent FCC feedstock, the naphtha produced from cracking is of low octane with high sensitivity (RON-MON spread).

Additionally, paraffinic crudes produce poor-quality, catalytic-reformer feedstocks which restrict the octane production from the reformer. At Eagle Point, these factors combined to severely strain the refinery's ability to produce motor gasolines from indigenous blendstocks at the lower levels mandated by the EPA.

From a cursory review, an immediate switch to a USY catalyst appeared to be the appropriate step. However, the Coastal FCC processes significant quantities of residual oil, and any change of catalyst would have to be consistent with a severe high-temperature, high-metal-on-catalyst operation.

In addition, because of the somewhat unorthodox configuration of the Eagle Point crude unit, crude running was very often restricted by the amount of resid which could be processed in the FCC.

The crude unit consists of three columns: atmospheric, gas oil, and vacuum, with the vacuum column being the unit bottleneck. As the crude charge became heavier in recent times, the limit of vacuum-column throughput has become more pronounced.

While resid cracking first started in the late 1970s, to maintain crude runs it had been necessary to route greater volumes of gas oil tower bottoms (vacuum tower charge) to the FCC, thus causing the critical link between the FCC and crude unit. Selection of a stable, coke-selective octane catalyst was of utmost importance.

Prior to switching to ROC-1DY catalyst, Eagle Point utilized a conventional high rare-earth-content Y zeolite catalyst. Residual content (1,000° F. + equivalent) in FCC feed averaged approximately 17 vol %, limited primarily by coke burning and regenerator temperature limitations.

The addition of ROC-1DY catalyst provided the necessary coke selectivity to allow additional resid cracking and overall higher unit throughput. Resid content in feed now typically ranges between 20 and 27 vol %, and an overall increase of approximately 15 vol % in unit charge has been observed.

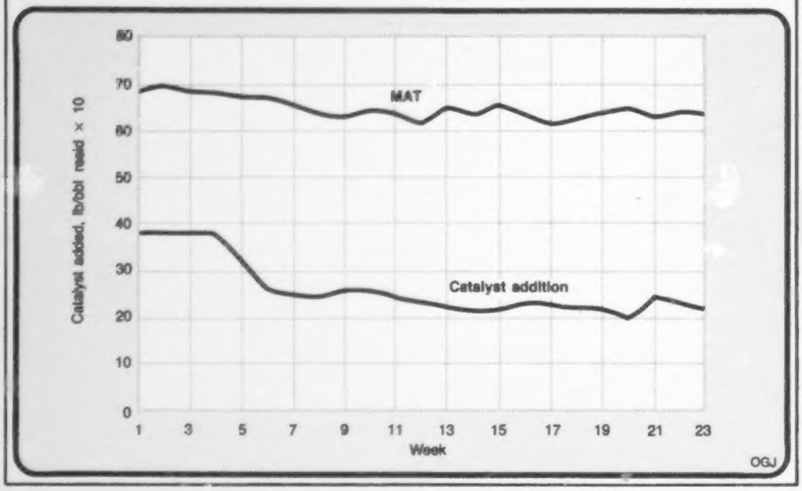
FCC-feedstock qualities are outlined in Table 1. The increase in charge was accomplished without deterioration of overall unit yields.

The new catalyst provides increased gasoline octane with significant coke reduction, remains stable, and limits dry-gas production. The attrition resistance and thermal stability of the catalyst has been excellent.

The effect on coke selectivity, dry

Fig. 5

## Fresh catalyst addition minimized



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gas, and regenerator temperature is shown in Fig. 1. The effect on resid in FCC fed is shown in Fig. 2.

Since the addition of ROC-1DY catalyst, the FCCU has been operated in both a maximum fuel oil (LCO) and maximum gasoline mode. To maximize the yield of middle distillate boiling range product, several steps were taken.

Reaction severity was reduced by lowering reactor temperature. Feed-preheat temperature was increased, and the quantity of heavy-cycle-oil recycle to the riser was also increased.

In addition to these adjustments, gasoline product was cut to 350° F. ASTM end point, adding to the total middle distillate yield. A summary of this middle distillate operation is shown in Table 2.

In addition to providing the coke selectivity, which allowed processing the increased quantity of resid and total charge, the ROC-1DY contributed to the two-number increase in both clear research (RON) and motor octane (MON) of the FCC gasoline. A second feature, the active matrix of this catalyst, has provided several additional benefits.

The most notable effect is the upgrading of heavy components into lighter boiling range products. During the LCO operation, which included additional nondistillable (1,000° F. +) material in the feed as well as reduced cracking severity, the total yield of decant oil increased only very slightly over the base operation, while the yield of LCO increased more than 10 vol %. This upgrading contributed to the significant improvement in gasoline MON clear.

As the demand for gasoline increased, the FCCU operation was adjusted to produce more naphtha-boiling-range product. The HCO recycle was reduced, the reactor temperature was increased, and the gasoline end point was raised to 420° F. The resulting yield distribution is shown in Table 2.

Even at the higher cracking severity required to produce maximum gasoline yield, the total feed rate was not reduced from the previous operation, also maintaining the 20-27 vol % vacuum resid in the combined FCC charge.

The coke and dry gas selectivities provided by the DY zeolite catalyst did not decline at this increased-severity operation.

The improvement in RON clear, normally associated with increased reactor temperature, was offset with the increase in gasoline end point for this operation.

It must be noted that the LCO is cut to a cloud-point specification rather than end point because of the paraffinic nature of both the feed and cycle oils.

With other catalysts, it had been virtually impossible to raise naphtha end point above 400° F. without adversely affecting LCO cloud point and the LCO/decant oil split.

In essence, the heavy gasoline acted as a cloud point cutter stock and economically could not be removed. Under the current operation, LCO cloud points have been reduced enough to allow production of FCC naphtha to any desired end point, constrained only by gasoline pool distillation specifications and the economics of upgrading the relatively low-octane, heavy FCC gasoline.

At 30¢/octane-barrel, the octane improvement alone from switching catalysts translated into a revenue improvement in excess $10,000/day.

The octane improvement experienced during operation with ROC-1DY is shown in Fig. 3.

The coke and dry gas selectivities, combined with the matrix properties, have provided a tool for controlling the two most limited factors, namely: reactor/regenerator heat balance and feed contaminant effects.

The coke and dry gas selectivities were demonstrated by increasing the feed rate and resid content in the feed, while not exceeding the existing metallurgical and mechanical limitations of the unit.

Eagle Point uses a metals passivator to control production of hydrogen. Nickel activity is Eagle Point's primary concern, because nickel accounts for approximately 85% of the metal on equilibrium catalyst. The effect of increasing nickel content on catalyst is shown in Fig. 4.

Eagle Point was able to take advantage of the increased metal tolerance of ROC-1DY to minimize addition of fresh catalyst, while maintaining the desired activity level, as shown in Fig. 5. Catalyst additions increased in rough proportion to the amount of resid cracking to maintain reasonable levels of metal contaminants.

Equilibrium catalysts are also added at times for metals control. Equilibrium additions typically average less than 25% of total catalyst makeup. ▪

## The authors...

**Lipinski**

**Wilcox**

John J. Lipinski is chief process engineer at Coastal Eagle Point Oil Co., a subsidiary of Coastal Corp. He joined Coastal in May 1985 after working with Texaco for 13 years at various process engineering assignments, and in refinery operations and environmental protection. Lipinski received a BS in chemical engineering from Stevens Institute of Technology, and he is a registered professional engineer in New Jersey.

Jack R. Wilcox is manager—technical services at Harshaw/Filtrol Partnership in Los Angeles. He has held the present position since May 1985.

Wilcox previously spent 15 years with UOP Inc. at various assignments in research and development, design engineering, and technical services. He received a BS in chemical engineering from the University of Illinois and is a registered professional engineer in Illinois.

# PCs are vital refinery balance and profit tools

**Richard A. Corbett**
Refining Editor

The U.S. refining industry is using microcomputers—commonly refered to as personal computers or PCs—in applications that pertain primarily to refinery planning, economics, scheduling, and process evaluation.

Typical calculations done on PCs include: material and fuel balances, heat balances, product blend optimization, crude oil scheduling, feed and product economics, and marketing studies.

Although each refinery will use the computer in a specific way dependent on the specific feedstock and product mix of that refinery, the generic applications are the same.

One of the most widely used pieces of software is the spreadsheet. Spreadsheet software has been adapted to most of the necessary analyses.

For overall refinery optimization, the use of linear programming (LP) techniques has been utilized by many companies. And although many LPs are too large for use on PCs, a few can run on them. Other systems use the PC in conjunction with a mainframe LP.

Suppliers to the refining industry, such as process engineering companies and catalyst suppliers, are also utilizing the PC to offer better products and services to the refiner. They are using PCs to perform process unit performance evaluations, catalyst analyses, material balances, and yields analyses for the refiner.

The use of computer-aided design and drafting (CAD) systems is finding its way into the refining industry, at both the refiner and supplier levels. Normally the playing field of large capacity mainframe computers, new software and CAD system designs are becoming increasingly availble for application to microcomputers.

Refining industry applications of personal computers are relatively new. Refiners began using them a little more than 5 years ago, but usage has grown dramatically since then.

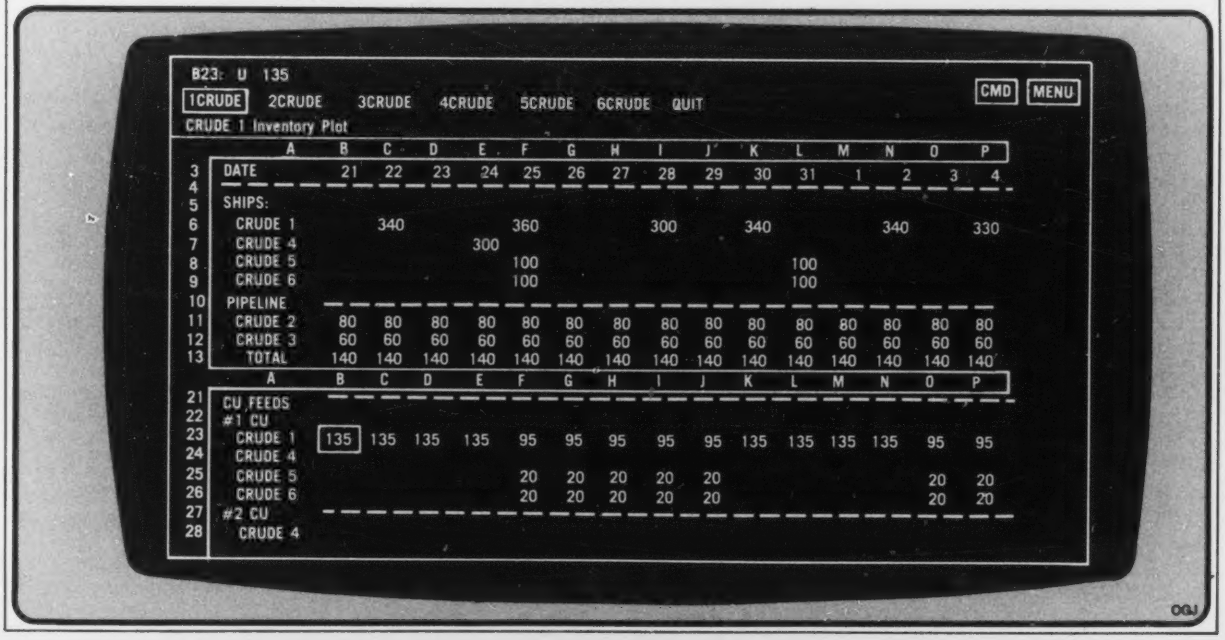
**Hardware.** Although a few variations in computer hardware are found, many refiners and suppliers have standardized on an arrangement consisting of the basic computer with 512-640 K RAM and a 10 megabyte hard disk memory.

Peripherals include a wide range of printers and plotters of the electrostatic, laser, and pen types. Almost all use color presentation because the cost addition for color is small compared to the overall investment in the equipment.

Most indicated that the cost of the hardware is justified by a single application. This means that there is usually excess capacity available for future applications. And since the system has been justified by the one applica-

Fig. 1

Typical screen display after executing plot macro



```
B23: U 135
1CRUDE  2CRUDE  3CRUDE  4CRUDE  5CRUDE  6CRUDE  QUIT                CMD  MENU
CRUDE 1 Inventory Plot
          A      B    C    D    E    F    G    H    I    J    K    L    M    N    O    P
 3  DATE        21   22   23   24   25   26   27   28   29   30   31    1    2    3    4
 4  - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
 5  SHIPS:
 6    CRUDE 1        340            360            300       340            340       330
 7    CRUDE 4                  300
 8    CRUDE 5                       100                           100
 9    CRUDE 6                       100                           100
10  PIPELINE     - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
11    CRUDE 2    80   80   80   80   80   80   80   80   80   80   80   80   80   80   80
12    CRUDE 3    60   60   60   60   60   60   60   60   60   60   60   60   60   60   60
13     TOTAL    140  140  140  140  140  140  140  140  140  140  140  140  140  140  140
          A      B    C    D    E    F    G    H    I    J    K    L    M    N    O    P
21  CU FEEDS     - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
22  #1 CU
23    CRUDE 1  [135] 135  135  135   95   95   95   95   95  135  135  135  135   95   95
24    CRUDE 4
25    CRUDE 5                        20   20   20   20   20                       20   20
26    CRUDE 6                        20   20   20   20   20                       20   20
27  #2 CU        - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
28    CRUDE 4
```

OGJ

Fig. 2

Crude-oil inventory from plot macro information

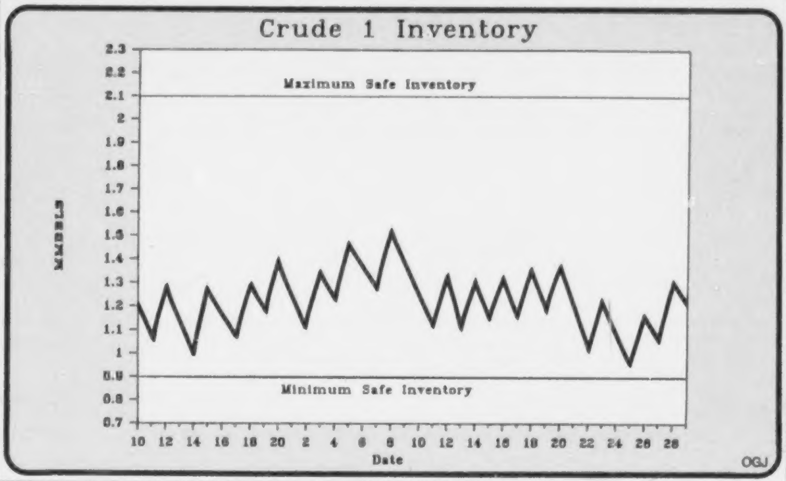
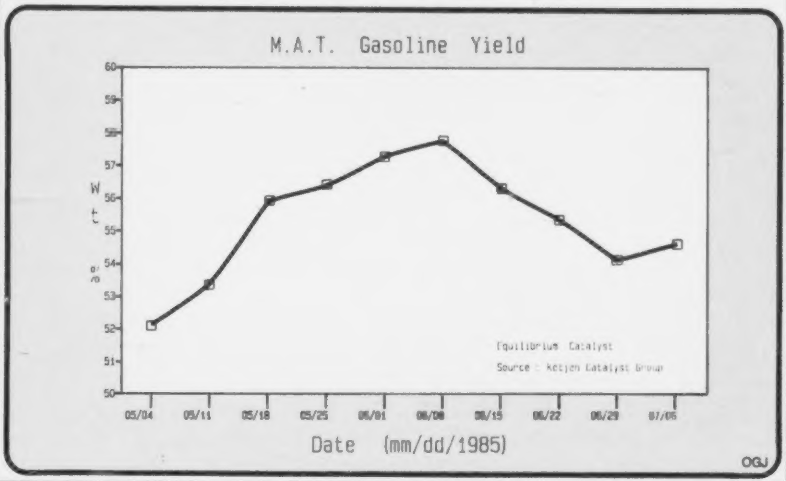


Fig. 3

Plot of MAT gasoline data from spreadsheet



tion, users are free to utilize the excess in any way that helps them with their individual jobs.

Now that hard disk memory is readily available at relatively low cost, most users will purchase the hard disk memory, knowing that at the beginning they won't use much of the memory, but they will have adequate room for expansion.

Also, much of the available software is composed on more than one floppy disk. This means the user must change disks often to run a program.

For instance, a popular spreadsheet software package can occupy as many as four to six floppy disks. With hard-disk memory, the entire contents of the floppies can be loaded into the memory and accessed by key strokes rather than changing floppies.

**Software**. There are many types of PC software available to refiners, but the most popular is the spreadsheet software of LOTUS 1-2-3.

The spreadsheet software allows calculations to be run in rows and columns, similar to traditional hand calculations that have been done for years in the industry, only much faster. This allows the user to investigate several options in a short time. Many "what-if" questions can be quickly answered, and more options can be considered, resulting in improved plant profitability.

Spreadsheet software is used for marketing analyses, feedstock cost analyses, material balances, product blending studies, and product margin studies. The spreadsheet also is used to compile reports of the results of the various calculations and studies.

Most PCs are also supplied with traditional software such as word processing for the day-to-day letters and memos required in a typical refinery. Wide use is made of graphics software.

For consistancy of results, PCs must operate from the same data. Software is available to allow communication between the various departments in the plant.

Also, the PCs are often required to access mainframe computers. For these cases, there is software that allows the PC to emulate a mainframe computer terminal—the mainframe thinks the PC is just another of its terminals.

## Refining applications

In today's volatile feedstock and product market, the refiner must respond quickly to changes that occur frequently and rapidly. To respond, the refiner must have timely and accurate data, and that data must be quickly analyzed. The personal computer is a valuable tool for month-to-month or short-term planning.

**Raw materials uses.** Crude oil scheduling is a popular use of the PC. At Chevron's refineries, the PC-based, crude scheduling aid is the simplest and most widely used aid, says Larry E. Justice, senior reseach engineer.[1] The crude scheduling aid is run on LOTUS 1-2-3 spreadsheet software.

At one plant, crudes are fed to four crude units, some of which must operate on blocked runs to meet specialty product demands. The operation coordinators must set crude blocks and rates to contain the crude in available tankage as well as meet the planned crude runs for the month.

The crude scheduling aid allows the coordinator to follow inventories for up to 45 days. The coordinator updates the schedule by loading the last schedule used, usually several days to a week old.

The coordinator updates the opening inventories along with month-to-date information on total receipts and crude runs. The coordinator then updates the crude receipt schedule, making any changes to the schedule since the last run, and adding the receipts for any days to the schedule.

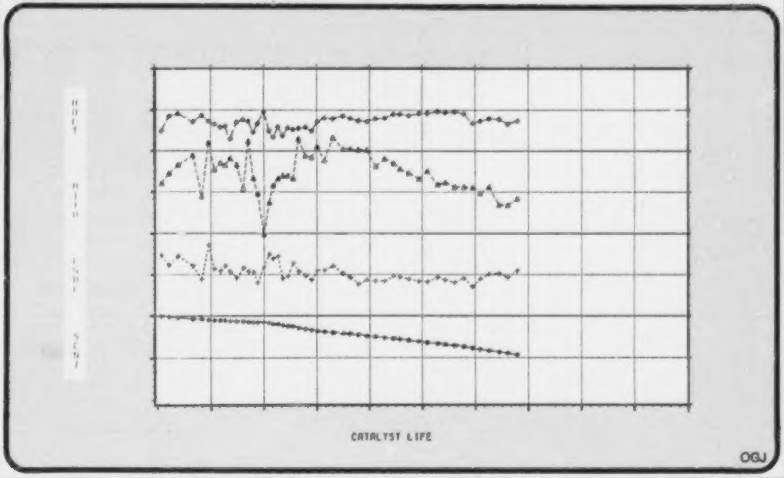
Next, the coordinator reviews the crude run portion of the schedule. This is where changes are made to stay within inventory limitations. The scheduling aid can display the inventory plots on a color monitor and the schedule on a monochrome monitor.

The coordinator can also see the effect of the planned runs on the average run for the month. These averages are targets that must be met to satisfy the operating plan for the refinery.

"An advantage of the LOTUS software is its ability to program macros,"

Fig. 4

Reformer operation tracked with PODS database



activities.

The model incorporates several options including summation of constraints to model the varying volume and octane of reformates from operation of a catalytic reformer, the capability to optimize the lead level in the leaded gasoline blends based on the price of lead credits, and the ability to simulate multi-period blending to further optimize a gasoline pool facing varying sales and production volumes, according to Schutt.

"The model has increased awareness of opportunity costs associated with sub-optimal blendstocks, stringent specifications and various grade volumes, as well as the effect of specialty products on the remaining pool," says Schutt. "This has resulted in increased profitability by giving the company greater control in areas previousy neglected."

"A gasoline-blending spreadsheet and a PC-based LP model that tracks gasoline blends and purchased olefins is used at Tenneco Oil Co.'s Chalmette, La., refinery," says Thomas N. Brock, administrative manager. "The users of the blending system are absolute converts. They take portable units home so that they have data needed to answer questions that arise nights and weekends."

**Other uses.** In addition to the planning and optimization applications in refineries, PCs are being used for training purposes, information distribution, marketing, and credit purposes.

La Gloria's credit department uses the PC to maintain current information on more than 400 customers. The PC is used to perform financial statement analysis on current and prospective customers. Analyses include cash flow trends and ratio analysis to evaluate financial performance, credit worthiness evaluations, and studies of overall stability of a company, according to Schutt.

Amoco is using PC-based graphics to generate illustrations for use with employee training films, according to Krueger. And computer graphics are used in many of the company's publications.

"Tenneco has a unique presentation system that puts graphics on a floppy and then runs the information through a black box that can be tied into a video projection unit," says Brock. "The projected image can be as large as 20-ft diameter, and it has very good resolution."

The projects scheduling group at Tenneco uses a PC system to schedule projects and monitor time and materials on major plant construction and revamp work.

"Using PCs, the group was able to cut 9 days off a major crude-unit turnaround," said Brock.

## Refining suppliers

Personal computers are becomming valuable tools for those companies that supply process engineering, systems, catalysts, and services to the refining industry.

PCs allow closer monitoring of process unit performance, quicker generation of proposed unit designs, more options to a given process design, and faster catalyst-study data transfer.

**Catalyst suppliers.** Some catalyst suppliers have found the personal computer valuable in checking the performance of a particular catalyst in a processing unit. The computer allows quick calculation of performance parameters, enabling the supplier to inform the refiner of imminent problems or corrective actions necessary says Justice. "Macros are a series of commands stored on the spreadsheet and recalled with a single keystroke."

With the macro, all graphs can be called through a user-designed menu to select a plot. Fig. 1 shows the screen display after executing the plot macro, and Fig. 2 shows a typical plot of a single crude's inventory.

"Daily inventory positions are tracked for all crude oil aquisitions on personal computers at La Gloria Oil & Gas Co., Tyler, Tex.," says Ken W. Schutt, manager of operations planning.[2] "The computers also assist with scheduling of crude deliveries into the refinery."

A hedging model is used by the raw materials and supply and distribution departments to monitor margins in the market place and identify attractive opportunities. And graphics generated from an historical data file of market indicators aid in identifying possible trends and other market analysis.

**Blending studies.** The personal computer is useful for optimizing product blends to obtain the best margin from available blendstocks. At Chevron, a short-term microcomputer LP has been developed to run calculations ranging from multicomponent blend optimization to extreme point refinery models.

"The LP uses the spreadsheet program for input," says Justice. "The user sets up a matrix on the spreadsheet in a row and column format and exits the spreadsheet. The user then runs the LP. The solution from the LP can be printed out or saved for input to a report-generating spreadsheet program."

Chevron's latest version of the LP can solve problems up to 250 columns wide by 200 rows long, using an IBM PC/AT or equivalent, according to Justice. The program uses a math coprocessor to speed calculations, and depending on the size and density of the matrix, computation time varies from a few minutes to more than 15 min.

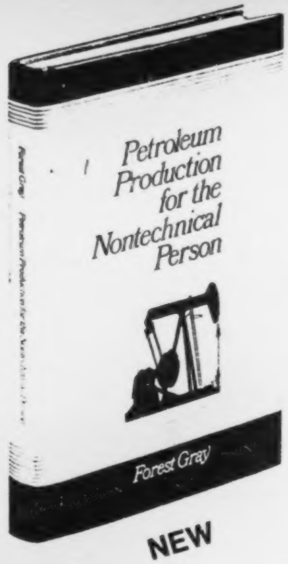
Chevron says the spreadsheet studies are easier to use than the mainframe LPs. And as the PC-based "barrel balance" spreadsheets become more sophisticated, they will be used for longer range studies.

"In contrast, Amoco's Whiting, Ind., refinery relies on the mainframe LP since it gives the true refinery optimum," says Paul Krueger, supervisor of computer maintenance. "Local access to the LP is sufficiently easy and if needed, the LP could run an optimization every 15 min."

La Gloria uses a BLEND model developed by Wright, Killen & Feldman Inc. The LP is a blending model used to improve gasoline blending

# PETROLEUM KNOW-HOW

## THE NO-PAIN WAY



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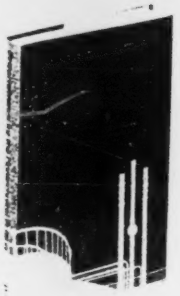

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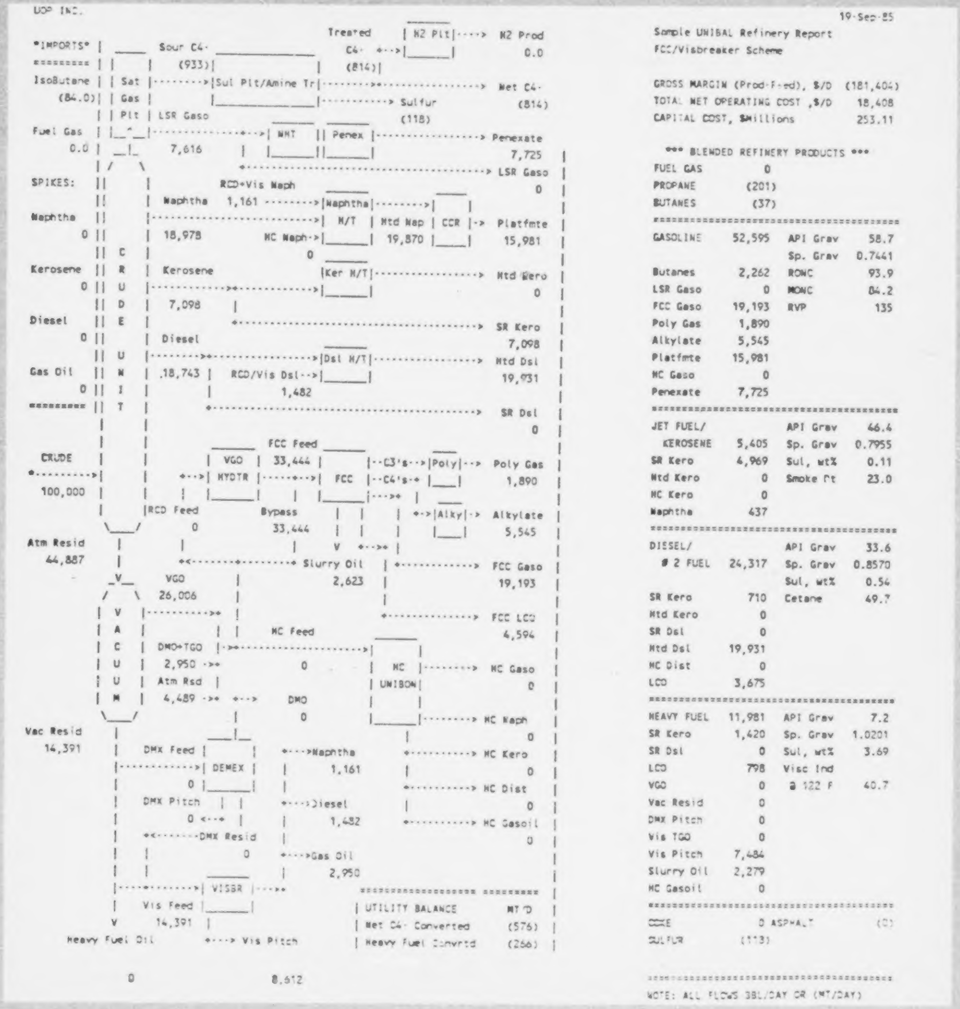
Fig. 5

## Refinery balance summary sheet*



```
UOP INC.
                                                       ______
                                            Treated   | H2 Plt|---->  H2 Prod
*IMPORTS* |  ____   Sour C4-  ______________    C4-  +-->|______|         0.0
========= | |    |    (933)|              |   (814)|
IsoButane | | Sat |-------->|Sul Plt/Amine Tr|-------->+----------------->  Net C4-
   (84.0)| | Gas |          |______________|----------->  Sulfur            (814)
         | | Plt | LSR Gaso                                 (118)
Fuel Gas  | |_^_|--------------+-->| NHT   || Penex |----------------->  Penexate
    0.0 |  _|_     7,616      |   |_____||______|                       7,725   |
        | /   \                 +---------------------------------------> LSR Gaso |
SPIKES:  ||    |             RCD+Vis Naph                                    0   |
         ||    | Naphtha  1,161 -------->|Naphtha|-------->|    |              |
Naphtha  ||    |------------------------>|  N/T  | Htd Nap | CCR |->  Platfmte  |
       0 ||    |  18,978         HC Naph->|______| 19,870 |____|     15,981    |
         ||  C |                      0                                        |
Kerosene ||  R |  Kerosene               |Ker H/T|----------------->  Htd Kero  |
       0 ||  U |----------->+------------>|______|                          0   |
         ||  D |  7,098    |                                                   |
Diesel   ||  E |           +---------------------------------------->  SR Kero  |
       0 ||    |  Diesel                                               7,098   |
         ||  U |-------->+--------------->|Dsl H/T|----------------->  Htd Dsl   |
Gas Oil  ||  N |  .18,743 |  RCD/Vis Dsl-->|______|                   19,931   |
       0 ||  I |          |        1,482                                      |
========= ||  T |          +---------------------------------------->  SR Dsl   |
          |    |                                                         0   |
          |    |           _____  FCC Feed  _____                            |
CRUDE     |    |          | VGO  | 33,444 |       |--C3's-->|Poly|-->  Poly Gas |
+--------->|    |     +-->| HYDTR |------+-->|  FCC  |--C4's-+ |____|      1,890  |
100,000   |    |     |   |______|      |  |_______|--->+  |                    |
          |    |RCD Feed          Bypass      |   |    | +->|Alky|->  Alkylate  |
          \____/     0            33,444      |   |    |    |____|     5,545   |
Atm Resid    |       |              |         V   +-->+ |                       |
  44,887     |       +<--------+-------+ Slurry Oil  | +------------->  FCC Gaso |
            _V__    VGO        |          2,623     |                 19,193   |
           /    \  26,006      |                    |                          |
          | V   |---------->+  |                    +------------->  FCC LCO  |
          | A   |            | |      HC Feed                          4,594   |
          | C   | DMO+TGO    |->+---------------------->|      |               |
          | U   |  2,950 ->+              0            |  HC  |-------->  HC Gaso |
          | U   | Atm Rsd  |                           | UNIBON|              0 |
          | M   |  4,489 ->+  +-->      DMO            |      |                |
          \____/              |          0             |______|-------->  HC Naph |
Vac Resid    |              __|__                          |                0  |
  14,391     |    DMX Feed |     |    +--->Naphtha          +----------->  HC Kero |
             |------------>| DEMEX |   |      1,161         |                0  |
             |           0 |_____|    |                    +----------->  HC Dist |
             |    DMX Pitch  |  |     +--->Diesel           |                0  |
             |          0 <--+  |     |      1,482          +----------->  HC Gasoil|
             |    +<--------DMX Resid |                                      0  |
             |    |            0      +--->Gas Oil                             |
             |    |                   |      2,950                             |
             |--+---------->| VISBR |--->+      ================== =========  |
             |   Vis Feed   |______|             | UTILITY BALANCE        MT/D  |
             V    14,391  |                      | Net C4- Converted      (576)  |
      Heavy Fuel Oil         +---> Vis Pitch     | Heavy Fuel Convrtd     (266)  |

             0                    8,612
```

```
                                     19-Sep-85
Sample UNIBAL Refinery Report
FCC/Visbreaker Scheme

GROSS MARGIN (Prod-Feed), $/D  (181,404)
TOTAL NET OPERATING COST ,$/D     18,408
CAPITAL COST, $Millions           253.11

  *** BLENDED REFINERY PRODUCTS ***
FUEL GAS          0
PROPANE       (201)
BUTANES        (37)
========================================
GASOLINE     52,595   API Grav      58.7
                      Sp. Grav    0.7441
Butanes       2,262   RONC          93.9
LSR Gaso          0   MONC          84.2
FCC Gaso     19,193   RVP            135
Poly Gas      1,890
Alkylate      5,545
Platfmte     15,981
HC Gaso           0
Penexate      7,725
========================================
JET FUEL/             API Grav      46.4
  KEROSENE    5,405   Sp. Grav    0.7955
SR Kero       4,969   Sul, wt%      0.11
Htd Kero          0   Smoke Pt      23.0
HC Kero           0
Naphtha         437
========================================
DIESEL/               API Grav      33.6
  # 2 FUEL   24,317   Sp. Grav    0.8570
                      Sul, wt%      0.54
SR Kero         710   Cetane        49.7
Htd Kero          0
SR Dsl            0
Htd Dsl      19,931
HC Dist           0
LCO           3,675
========================================
HEAVY FUEL   11,981   API Grav       7.2
SR Kero       1,420   Sp. Grav    1.0201
SR Dsl            0   Sul, wt%      3.69
LCO             798   Visc Ind
VGO               0    @ 122 F      40.7
Vac Resid         0
DMX Pitch         0
Vis TGO           0
Vis Pitch     7,484
Slurry Oil    2,279
HC Gasoil         0
========================================
COKE              0 ASPHALT          (0)
SULFUR        (113)


========================================
NOTE: ALL FLOWS BBL/DAY OR (MT/DAY)
```

* From UOP's UNIBAL material and utility balance program

OGJ

to maintain top unit performance.

At Katalistiks Inc., personal computers are used to evaluate the performance of fluid catalytic cracking units in which Katalistiks' FCC catalysts are used.

The PCs provide heat and utility balances, component breakdowns for the FCC operation, and are used for microactivity test (MAT) calculations and presentation of results.

"Katalistiks began using PCs to save service engineers' time needed to perform the tedious calculations required for the evaluations," says Dennis Michaelis, director of technical services. "The service engineer now has more time to work with the customer and the customer gets the evaluation results much faster.

"Prior to the use of PCs, the service engineers had to rely on data that could be as much as a month old," said Michaelis. "And it was difficult to get the engineer to do the necessary calculations."

Katalistiks has experimented with direct communication between the refiner and the catalyst facility, and some success was noted. But security concerns and difficulty with clear phone lines has limited these communications.

The normal procedure is to have the refiner Telex the data to Katalistiks, where the evaluations are performed, and then Telex the results back to the refiner. This can normally be done in a matter of days, according to Michaelis. The evaluations are done on an IBM PC using LOTUS 1-2-3 spreadsheet software.

"Personal computers are relied on heavily to report lab tests of FCC equilibrium catalysts at Akzo Chemie Ketjen Catalysts in Pasadena, Tex.," says Pankaj Desai, service engineer. "For example, the lab uses the PC to perform the necessary calculations for MAT tests run on customer catalysts. Reports are prepared from the MAT results and presented both in tabular form and graphic form." Fig. 3 shows a typical graphical output of the MAT test results.

**Process suppliers.** "UOP Inc. began using personal computers for its internal design and engineering functions," said Richard Silverman, project manager. "But refiners became aware of the calculations run and data generated for UOP's licensed processes, and began requesting copies of the information. UOP realized this could be a valuable service to offer refiners."

One service offered by UOP is its PODS or Platforming Operating Database Service. The system allows UOP and the refiner to closely follow the operation of licensed catalytic reforming units. Actual unit performance can be compared to predicted values (Fig. 4).

Another service offered by UOP is its UNIBAL system. The system runs complete refinery material balance calculations on a personal computer. Fig. 5 shows a summary sheet of data calculated.

Process simulation is another important use for PCs at the supplier level of the refining industry. PC-based process simulators are used to help train and familiarize new process operators.

"Stratco Inc., Kansas City, offers an alkylation unit training simulator to help train new operators of the system," says Eileen Prohaska, process engineer. "The advantage of the simulator is that operator training can begin before the unit is completly installed. This means that operators can be familiar with the operation of the unit before start-up."

Kellogg Plant Services, Houston, can supply custom designed process simulators for use as training aids on Kellogg process units. A feature of the simulators is that they can be designed to duplicate the appearance of the actual process control panel, according to Dr. S. Madhavan, manager, technical services.

Kellogg has also developed a PC-based, custom-designed plant maintenance management system that includes workorder tracking, nameplate tracking, equipment history, and job planning.

## CAD systems

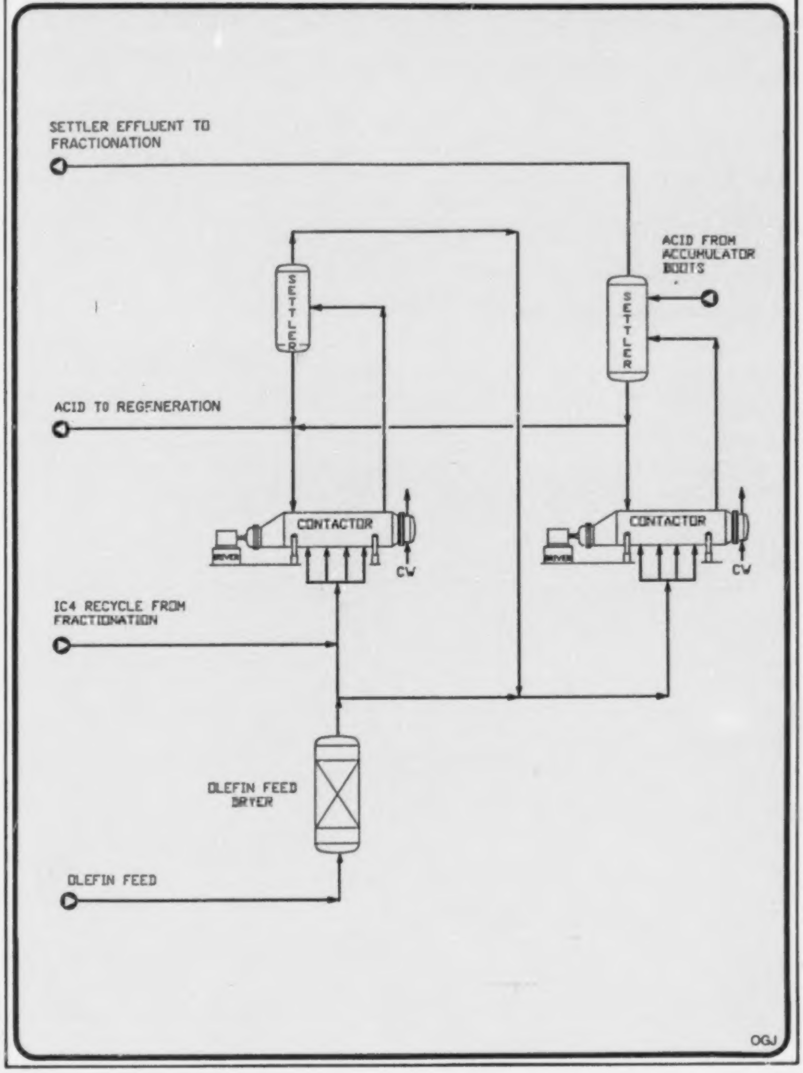
Refining industry use of microcomputer CAD systems has been limited because most CAD systems are designed for mainframe and minicomputers. A typical refinery seldom needs the power, nor can it justify the cost, of a complete plant design CAD system such as those found in large engineering firms.

What the industry needs is a system that can perform the necessary drafting needs of the refinery. These needs include generation of process flow diagrams (PFDs), process and instrument diagrams (P&IDs), electrical diagrams, and piping layout drawings. Many refineries do not have a full drafting staff to accomplish these tasks.

La Gloria recently ordered a CAD system that will vastly reduce drafting time currently being expended. Ken Schutt says, "This time is especially valuable since no draftsmen are employed at the refinery and this work is either contracted or performed by company engineers."

Fig. 6

P&ID generated by Stratco's 2D CAD system


SETTLER EFFLUENT TO FRACTIONATION
ACID FROM ACCUMULATOR BOOTS
SETTLER
SETTLER
ACID TO REGENERATION
CONTACTOR
CONTACTOR
CW
CW
IC4 RECYCLE FROM FRACTIONATION
OLEFIN FEED DRYER
OLEFIN FEED
OGJ

"The main benefit of the CAD system will be the ability to keep plant drawings up to date," says James W. Jones, manager of engineering and planning at La Gloria. " There won't be much savings when making new drawings, but the system will save considerable time when revisions are necessary.

"It has always been a problem for refineries to keep up with drawing changes caused by plant upgrades and equipment and control changes. One important use will be keeping plant electrical ladder diagrams updated."

La Gloria's system is a 2D system that will run on existing IBM PC/XT's utilizing 10 megabyte hard disk memory. The software for the system cost about $2,000; the plotter (the most expensive part of the system) about $10,000. But it will handle C and D size drawings.

Phillips Petroleum Co. recently installed a CAD system at its Sweeny, Tex., refinery, say M.A. Woolbert, information services manager, W.I. Haring, design engineering supervisor, and R.S. Bennett, maintenance special project engineer.[3]

"The CAD system that is both inexpensive enough and powerful enough for the plant environment is something that is relatively new on the market," they say. "The advent of super microcomputers has made it possible."

The Phillips system consists of four work stations, two 70-megabyte disk drives, a check plotter, a 24-in. electrostatic plotter, a 300-megabyte disk for on-line storage, a tape drive for archive and back up, and a 1-megabyte network process server. The system is a distributed logic system, and each work station is a 1.5-megabyte computer in itself.

"The more common solution to the CAD problem has been a shared logic system (i.e., a giant mainframe central computer with terminals hung off it)," says Phillips. " Frankly, we couldn't afford a shared logic solution to the CAD problem. In addition, we felt that the solution was fraught with the usual mainframe pitfalls such as running out of capacity and being forced to have to ask for money for CPU upgrade."

Equipment suppliers are using microcomputer CAD systems to enable them to quickly submit drawings to their customers. And when the customer asks for changes to the design, the supplier can respond much faster. CAD designs also give the customer the ability to review several different options in a short time period.

Stratco uses a 2D CAD system with IBM PCs to produce drawings of its alkylation units. The system makes P&IDs, PFDs, and equipment sketches for submittal to the customer, according to Eileen Prohaska. Although the system is a bit slow, it produces good-quality drawings. Fig. 6 shows a P&ID generated by the CAD system.

**Future.** Most of the future uses of PCs in the refining industry consist of more of the day-to-day calculations necessary to keep a refinery running at peak efficiency. These uses will grow as engineers become more and more familiar with the capabilities of the available software.

Hardware is proving satisfactory for current uses and will probably be adequate into the near future.

Interfacing with mainframe computers and networking microcomputers are areas where more advances will be made. Amoco would like to see software available that would allow networking its microcomputer system on a multiuser basis, according to Krueger.

"Chevron is evaluating an LP interpretation system called WHATS BEST. The system will interface a mainframe LP with a spreadsheet program," says Justice. "It will read the LP output and present the optimum solutions on the spreadsheet with a single keystroke." This is also an area for the new generation of intelligent or expert systems when they become available.

Both Katalistiks and Akzo Chemie see more use of telecommunications between refiners and catalyst suppliers. They also feel that the security problems will be overcome. This will provide faster transfer of catalyst and unit performance evaluations.

There's no doubt that microcomputers have helped refiners and suppliers meet the increasing competitive demands in today's refining market. They have freed engineers of tedious hand calculations, provided quick solutions to feedstock and product mix problems, and put a large amount of data at fingertip availability.

"There are still, however, no guarantees; personal computers and planning systems alone will not make a company more competitive or ensure its profitability," says Ken Schutt. "But without faster reaction time, improved communications, and unified management direction, failure in today's environment is almost certain."

Personal computer use might very likely mean the difference between profit and loss for some refiners.

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# Simulator a key to successful plant start-up

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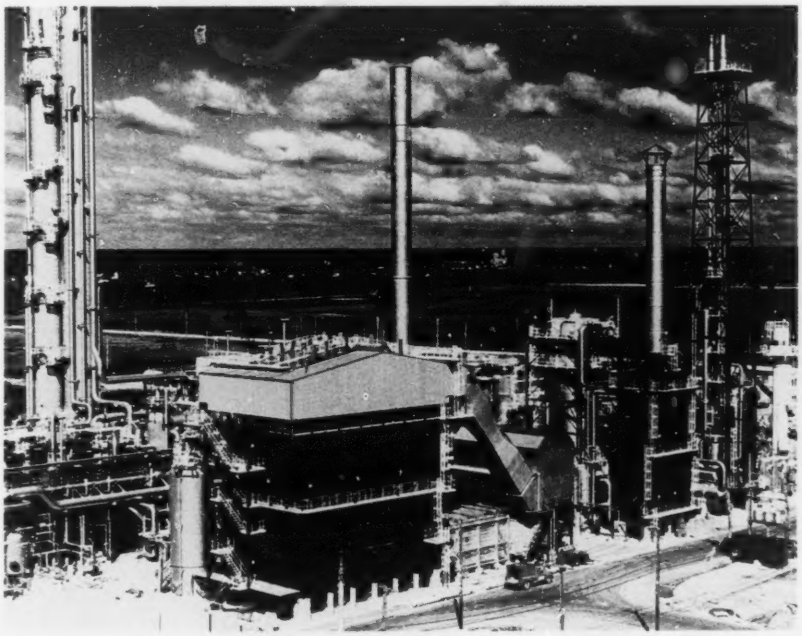


**C-I-L's Ammonia II plant**, located along the St. Clair River at Courtright, Ont., uses ICI's newest AMV ammonia technology. This first-of-its-kind plant is designed to produce 1,200 tons/day of anhydrous ammonia, consuming 305 therms of natural gas/ton (Fig. 1).

**A** sophisticated, real-time process simulator and a smoothly functioning engineering and construction team were key factors which contributed to a flawless and near world record (43-hr) start-up of C-I-L's AMV Ammonia II plant in Courtright, Ont. (Fig. 1).

Commissioned in August 1985, the 1,200 ton/day plant uses new, energy-efficient technology (Fig. 2) developed by C-I-L and its British-based parent, ICI. The plant is controlled by a combination of Honeywell TDC 2000 and a C-I-L-developed Cygnus supervisory control system (Fig. 3).

The simulator contains computer-based models of the actual ammonia plant units and control systems. Similar to systems used in the airline and aerospace industries, it enables trainees to practice operating the plant, in normal as well as critical operating conditions, without risk.

Commissioning manager Bill Taylor says that significant contribution to the success of the start-up was made by the extensive pretraining of operating personnel using the simulator, which exactly duplicated the operation of the plant in real-time response.

Training involving more than 100 simulated trip situations eased operators' transition from pneumatic to Cygnus and the TDC 2000 video display control system. Without the simulator, it could take 10 years of on-the-job training and plant experience to acquire the same skills.

**Simulator justification.** Real-time, dynamic simulators are recognized as the ultimate tool for training, evaluating student performance, and design /engineering of complex systems. Simulators have been used extensively in the airline industry and for military applications since as early as the 1940s, the Link trainer being one of the earliest and most widely used.

Although recognized for their ability to safely train for. hazardous or emergency situations, simulators are justified differently in different industries. While regulations may dictate use, economic payback is also an important factor.

The airline industry makes extensive use of simulators for both pilot training and regular requalification of flight staff. Even though the government requires simulator training, and it is a much safer training method, justification can also be based on simple economics: aircraft simulators cost far less to operate than the actual equipment. Significant savings are realized in fuel alone.

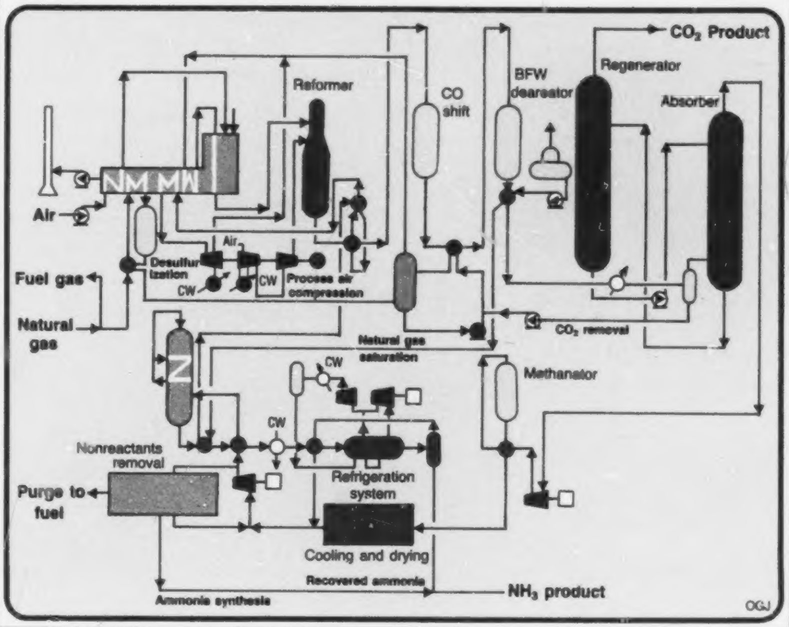
Government regulations also contributed to increased use of large-scale, multimillion-dollar simulators for fossil and nuclear power plants. Safety notwithstanding, these expensive, hardware-intensive systems could also be cost-justified due to the nature of the power industry

When a utility is unable to supply its customers, it must purchase electricity from other sources, usually at higher rates. Studies quickly showed that an expensive training simulator could be justified on the basis of reduced outages caused by operator error.

The popularity of general-purpose training simulators in the process industries paralleled increased construction activity in the late 1970s and early 1980s. A shortage of qualified operators, coupled with new control system technologies, demanded a training tool which could raise the

Fig. 2

AMV ammonia process flowsheet



experience and proficiency levels of trainees in the fastest possible manner. Simulator cost was secondary when compared with the alternative of being unable to operate the plant due to lack of trained personnel.

Recently, high-fidelity simulators used for operator training, plant design, and control strategy evaluations have become less expensive. Improved computer price/performance ratios and software emulation of control systems have significantly reduced the cost of hardware required for a simulator. In addition, the labor needed to program detailed plant dynamics has been streamlined by the advent of user-friendly model development languages.

However, even with substantial savings to be gained through use of simulators for engineering and design applications, the primary justification many companies use for buying process simulators is intangible: better operator training and the resultant safer plant operations. The economics of improving plant production by reducing downtime from upsets is normally significant, but usually difficult to quantify because data on plant performance vs. training are not available.

Thus, only after the simulator has been used and plant performance evaluated can the specific economic and training benefits derived for a particular plant be determined. Even then, the relationship of plant performance to simulator training may still be difficult to quantify unless specific objectives or targets have been detailed in advance.

in the case of C-I-L, the new plant technology, digital control system, and inherent complexities of running a highly interactive ammonia process played a key role in justifying the simulator. C-I-L documented the specific simulator benefits and quantifiable objectives they intended to use in justifying procurement of their system. After plant start-up, these factors were reviewed.

This enabled C-I-L to identify specific operator activities and plant performances which were impacted by development and use of the simulator.

**Training requirements.** Running an ammonia plant properly requires highly developed operating skills. These skills depend on detailed insight into the process as well as the dynamic operating characteristics of the plant. Proficiency in the use of the control systems which govern plant operation is also required.

Ammonia plants being designed today are significantly different from older ones. Most new ammonia technologies offer operating efficiencies far greater than in the past. They exhibit a high degree of interaction between sections of the plant.

Most new plants also utilize distributed digital instrumentation systems, in contrast to the older analog panelboard systems. Thus, the operator must be trained to operate a more complex and dynamically interactive process through a CRT-based control system with a totally different man/machine interface.

Although the trainees at C-I-L had extensive ammonia plant experience, none had used distributed control systems such as the TDC 2000 or Taylor MOD 300. Thus, a simulator was selected both to ease the transition from pneumatic to digital controls and to learn the process responses characteristic of the new plant technology.

Another objective was to use the system for ongoing training after the initial period of start-up training. Periodic refresher training was planned to keep operator proficiency levels high by practicing events which occur infrequently, such as upsets or emergency conditions. The simulator's design also had to provide for keeping the system current with actual plant and control system configuration.

Overall, the simulator would perform several categories of training. It would:

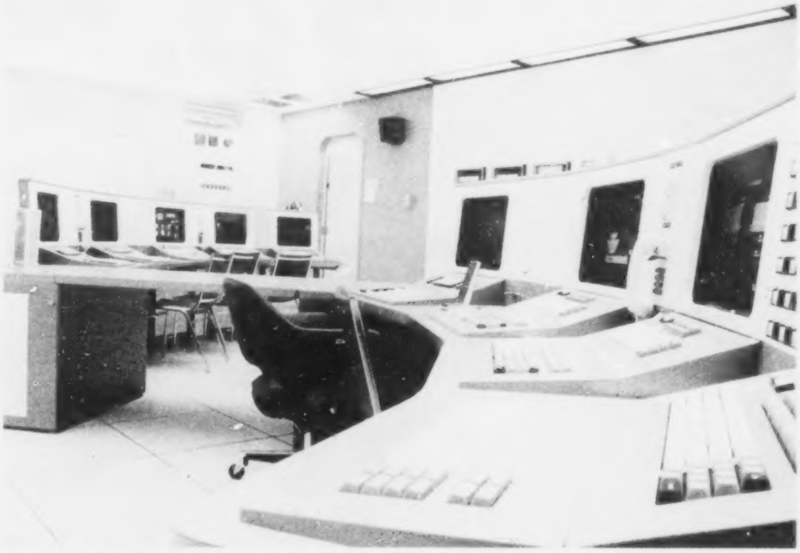
- Teach the operators the basic skills necessary to perform control actions and obtain information through the use of displays and keyboards.
- Familiarize the operator with normal operating values for all the fundamental indications and control loops.
- Provide experience and exposure to a set of typical process upsets and equipment malfunctions.
- Permit operators to learn and practice correct start-up and shutdown procedures.

**Other considerations.** C-I-L considered other factors in determining the value of a simulator. Insurance surveys estimate that approximately 25% of losses from accidents in the petrochemical industry are the result of process upsets and human error. Even with superior process design and protection logic, the ammonia unit is a complex plant with unique operational features. The simulator could provide a key link between operator training effort and a subsequent reduction in the number of plant trips and accidents.

Although designed for training, users of simulators have found that process design and control strategies can be verified when a high-fidelity model is used. Preliminary controller tuning and review of alternate control strategies could be tested on the simulator before they were implemented. Also, equipment and vessel sizing could be evaluated before plant construction.

As a result of a projected reduction in plant trips, better operations due to higher operator proficiency levels, and potential benefits from a verified control strategy, C-I-L estimated that 2 weeks worth of production would be gained in the initial months of operation. And because of ongoing training, one 3-day outage/year would be eliminated. The result would be a production increase of approximately 1%/year. Typically, a shutdown costs approximately $100,000, excluding lost production.

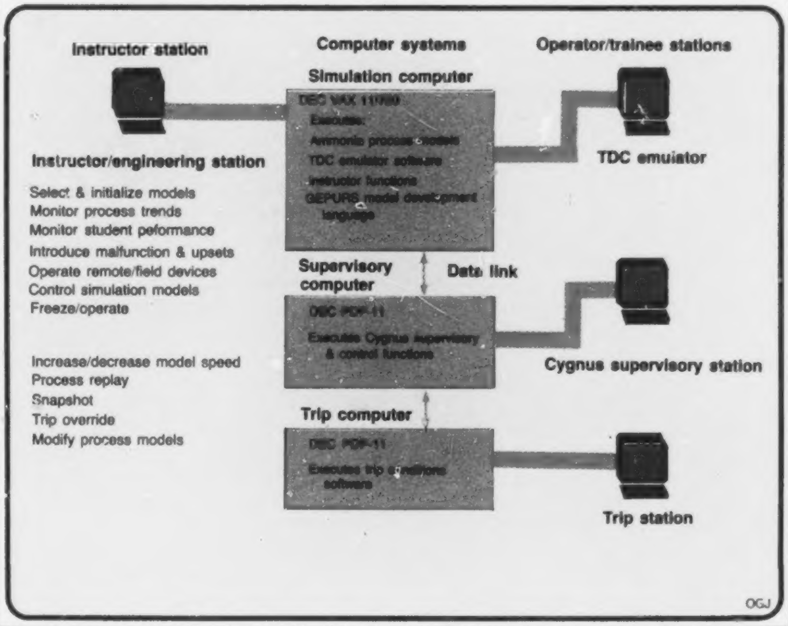
Based on these factors alone, the total discounted cash flow return on the simulator investment was estimated at nearly 80%.



**Ammonia plant control** room, with primary and secondary control stations, houses the Honeywell TCD 2000 and C-I-L developed Cygnus supervisory control systems. Nearly all of the plant's instrumentation is operated from these control systems (Fig. 3).

Fig. 4

C-I-L ammonia plant simulator


Instructor station
Computer systems
Operator/trainee stations
Simulation computer
DEC VAX 11/780
Executes:
Ammonia process models
TDC emulator software
Instructor functions
GEPURS model development language
TDC emulator
Instructor/engineering station
Select & initialize models
Monitor process trends
Monitor student peformance
Introduce malfunction & upsets
Operate remote/field devices
Control simulation models
Freeze/operate
Increase/decrease model speed
Process replay
Snapshot
Trip override
Modify process models
Supervisory computer
Data link
DEC PDP-11
Executes Cygnus supervisory & control functions
Cygnus supervisory station
Trip computer
DEC PDP-11
Executes trip conditions software
Trip station
OGJ

**Simulator description.** The simulator (Progres 3200, designed and engineered by Combustion Engineering Simcon Inc., Bloomfield, N.J.). consists of (Fig. 4):

- GEPURS simulation software
- Operator-trainee stations
- Instructor station
- Simulation computer.

All of these components were integrated and tested before final installation and site acceptance testing at C-I-L's Lambton Works in Ontario.

At the center of any computer-based application is the software which drives the system. High-fidelity AMV ammonia process simulation models were developed using GEPURS, an interactive program development language. It is structured in a block format which facilitates the development of detailed, dynamic process models.

Much of the model development effort is in debugging and fine tuning process models. Once the initial mathematical plant model equations are designed, the GEPURS online, interactive features permit model development and modification without recoding or recompiling after every change.

The GEPURS/user interface was designed to minimize the amount of Fortran coding required to develop dynamic plant models, yet provide maximum flexibility during the development and debugging phases. The interactive capabilities of GEPURS significantly decreases the development effort over the code, compile, link, and run approach.

In the block-structured approach, blocks are created from the existing math or process algorithm library. Physical and thermodynamic coefficients are entered to make the model match the actual plant parameters. The blocks are then linked together. All this is done on a CRT terminal, interactively and online.

After the model data base is generated, individual block performance is checked, as well as the interaction with other blocks. During the checkout and debugging phase, the engineer can:

- View and change parameter values
- Add or modify the process models
- Change the execution sequence and rate of specific blocks
- Place individual blocks on or off scan.

The result is a completely interactive, near-replica model of the AMV process. The pressure, temperature, flow, and level indications and controllers respond almost exactly as the actual plant equipment.

Replicating the plant responses had advantages over simpler, more generic process simulators that were considered: "We needed to win the confidence of the operator-trainees," said Dave Miller, simulator project coordinator for C-I-L. It soon became obvious that the students, some of whom had more than 12 years of ammonia plant experience, needed to believe that the simulator responded the same as the actual plant. This belief translated into more attentiveness and an increase in learning speed.

"We have already had several operators request additional simulator time, now that the plant commissioning is complete," says Verne McAlpine, senior operations supervisor at C-I-L. He is responsible for supervis-

**Instructor and trainee** can use the simulator to practice start-up, shutdown, and a variety of operating conditions that could be encountered in the ammonia plant. The student's console is a near replica of the actual operator's station (Fig. 5).

ing much of the training.

Refresher training, to let operators practice procedures which can't be done while the plant is running smoothly, will be scheduled. The detailed plant model will keep operators challenged and their operating skills sharp.

There is another advantage in having a near-replica plant model. C-I-L's engineering staff can tune and modify the model as required, to coincide with physical changes in the plant or to conform to any subtle, dynamic responses of the plant that were not recognized earlier and that differ from those of the model.

The project coordinator points out that the plant is continually changing and being modified to improve performance. GEPURS will be used to keep the simulator models and control system up to date.

**Emulated TDC 2000.** Today's state-of-the-art simulators emulate distributed control systems using software rather than interfacing to expensive instrumentation hardware, which can also restrict certain training capabilities. The TDC emulator uses a color CRT (Aydin) and TDC 2000 basic operator station keyboard (Fig. 5), specially interfaced to the computer. All displays, keyboard commands, and control functions are performed by the computer.

The trainee uses this station to observe and control the simulated process in virtually the same manner as he would use actual plant instrumentation. The 200 group displays, 8 process variables/group, used in the real control room were duplicated on the emulated TDC 2000 control system.

To add to the realism of the operator-trainee station, a Cygnus-based supervisory control station and a computer-based plant trip station were included. This replica of the control room, available before start-up, enabled C-I-L's engineering staff to perform a thorough evaluation of the actual control system configurations.

In addition to the engineering staff, the operations staff also benefited. Operators were able to become familiar with the large number of TDC displays and Cygnus graphics before actual start-up.

**Instructor station.** A separate station allows the instructor to control the training session as well as monitor the ammonia process and the student's performance. The availability and functions of this station give the training simulator capabilities not available on simulations used purely for design and control studies. A user-friendly interface minimizes the instructor's need to understand computers and maximizes the training capabilities available.

The instructor station consists of a color graphics terminal and a function button keyboard. Menu-driven displays (Fig. 6) allow the instructor to select, start, and freeze the process models. Other displays permit a view of the simulated process conditions in tabular, trend, and graphic P&I forms. All have real-time data continuously updated from the plant model.

Other instructor station functions include:

- Malfunction introduction: Both discrete and variable malfunctions can be initiated by the instructor. These functions can be time-delayed. Variable malfunctions, reduction in catalyst activity, or exchanger fouling for example, can be ramped.
- Operation of remote functions: The instructor performs the duties of the outside or field operator by viewing and changing the status of the remote functions through displays and the keyboard.
- Store/recall of process conditions: The instructor may store the current process conditions, called snapshot, on disk and recall them as the starting point in future training sessions. Snapshots are usually stored for intermediate start-up conditons, as well as various design and critical operating modes of the plant.

The instructor can replay the simulation session for instructional purposes. He can also bypass or deactivate trip logic.

These advanced training features were never fully utilized during start-up training. In the time available, C-I-L had to concentrate on familiarization with the control system, understanding plant responses and practicing plant start-up. More of these training features will be used when operators return to the simulator for additional training.

**Simulation computer.** The computer configuration for the C-I-L simulator consists of:

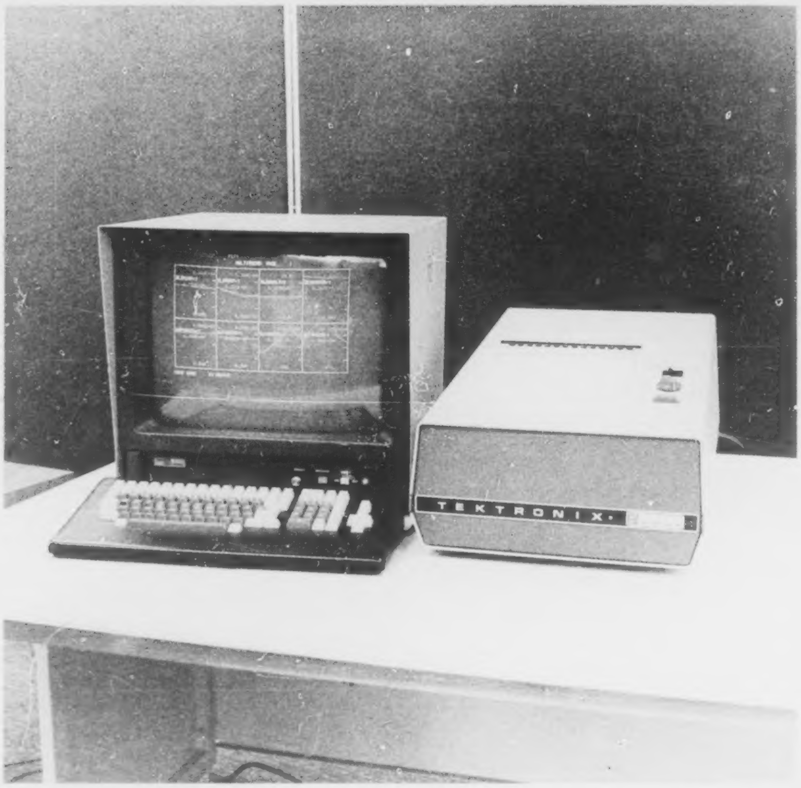
- DEC VAX 11/750 simulation computer
- Two PDP-11 supervisory and trip computers
- A data link between the central processing units (CPU).

Industry-wide, the price/performance ratio of high-performance minicomputers has dramatically improved. This makes process-intensive applications such as real-time simulators more affordable.

The VAX 11/750 drives the simulator by executing the process models, the emulated controls, and screen displays, and the instructor station requests. It utilizes a 32-bit processor, floating point accelerator, and Winchester disk drive system. The computer is also equipped with an Ethernet communications controller to permit fast data transfers to the supervisory computer via DECnet/VAX protocol.

The supervisory computer, containing the Cygnus control system, and the trip computer consist of PDP-11, 16-bit processors with associated peripherals. They also include Ethernet communications controllers.

The data link between the simulation CPU and the supervisory computer consists of a DEJNA-AA in the VAX 11/750 and a DEQUNA in the PDP-



**Instructor's station** is used to control the training session from menu-driven displays. The instructor may introduce malfunctions, save plant conditions, and view real process trends and conditions (Fig. 6).

11. The controllers are interconnected via Ethernet communication cables and communicate synchronously at a 10 Mb baud rate.

For all practical purposes, the supervisory and trip systems function as if they were receiving real plant information.

As an added benefit, the capabilities of the VAX computer are being used for applications other than simulation, Dave Miller indicated. When the system is not being used for training, it can perform engineering calculations. While these applications are relatively minor, the capability of using the computer for general purposes reinforces the flexibility of the system.

**Start-up results.** Delivered in November 1984, the simulator was used through March 1985 for operator training. The overall program combined the simulator with traditional classroom and on-the-job training over 12 months starting in April 1984. For the actual training, each operator received approximately 100 hr of formal instruction on the simulator and approximately 40 hr of informal time.

Simulator training, coupled with extensive unit pretesting, enabled a plant start-up in 43 hr. On-spec ammonia was produced just 3 hr later. This alone may have justified the cost of the simulator several times over.

The benefits derived from the simulator development and highly trained operating crews were evident both before and immediately after plant start-up.

During development of the detailed plant models, work on the simulator helped identify a design problem. Simcon's process modelers had difficulty maintaining stable operation of a steam turbine which contained complex governor controls. Highlighting this problem on the simulator expedited redesigning of the controls by the equipment manufacturer. If not corrected, the problem would have resulted in start-up delays.

C-I-L definitely feels that the simulator helped teach operators to identify plant problems during the first few critical minutes of an upset and take corrective actions before shutdown occurred. Once the plant is down, it takes 24 hr to get back onstream.

A few hours on the simulator is equal to several years of actual plant experience. The simulator allowed trainees to learn and try things that couldn't have been done using conventional training tools.

During the first 2 months of operation, C-I-L documented successful resolution of several incidents which could be directly attributed to the training given to operating crews. In fact, some of the conditions were encountered and practiced on the simulator during the start-up training sessions.

## The author...

**Pathe**

David C. Pathe is a consultant based in Sea Girt, N.J. He specializes in dynamic process simulation for design, control, and training. He began his career with Exxon, developing computerized, steady-state simulation programs for process design and engineering applications. He also worked for Autodynamics in designing, developing, and marketing dynamic simulation programs and computer-based training systems for the process industries.

- The ammonia recycle compressor tripped due to a gas leak on the instrument tubing, which also resulted in the synthesis gas compressor shutting down. Both machines were restarted from this condition with a production loss of only 20 tons.
- The ammonia refrigeration compressor tripped on three occasions, yet was restarted each time with only moderate product losses. Correct operator action prevented a complete plant shutdown.
- Process air trips occurred four times. They were corrected with no noticeable production loss.
- The synthesis gas dryer was successfully bypassed to account for a gas leak, with no production losses.

In the future, the simulator will be used to train all new operators and for periodic refresher training of experienced staff. It will also be used to fine tune operating procedures and evaluate alternate approaches. New procedures can be tried and practiced safely on the simulator without risking plant equipment or upsetting actual plant operations.

C-I-L feels that purchase of the simulator was more than justified. Less than 0.5% of the plant's capital investment was spent on people and training equipment.

**Acknowledgments.** The author thanks Combustion Engineering Simcon and C-I-L for their assistance and support in generating this article.

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# Dynamic simulation gives 20-20 foresight

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Dynamic simulation is being increasingly recognized as a viable tool for system analysis and design. Its use by Mobil Research & Development Corp. (MRDC) has grown steadily.

Applications (Table 1) fall into three major categories:

- Support of major capital projects, mostly in the form of high-fidelity models capable of answering many of the "what-if" questions which arise during the engineering design, construction, and commissioning phases of a project.
- Simulators for operator training, which have been acquired for an increasing fraction of both new and existing facilities over the past 10 years.
- Solution of operational problems, evaluate process changes, and in debottlenecking studies of existing facilities.

A number of dynamic simulations have been done by contractors or system vendors. MRDC involvement was limited to review and/or acceptance of the work. MRDC did not write any of the training simulator programs, for example, although its inputs often influenced their development.

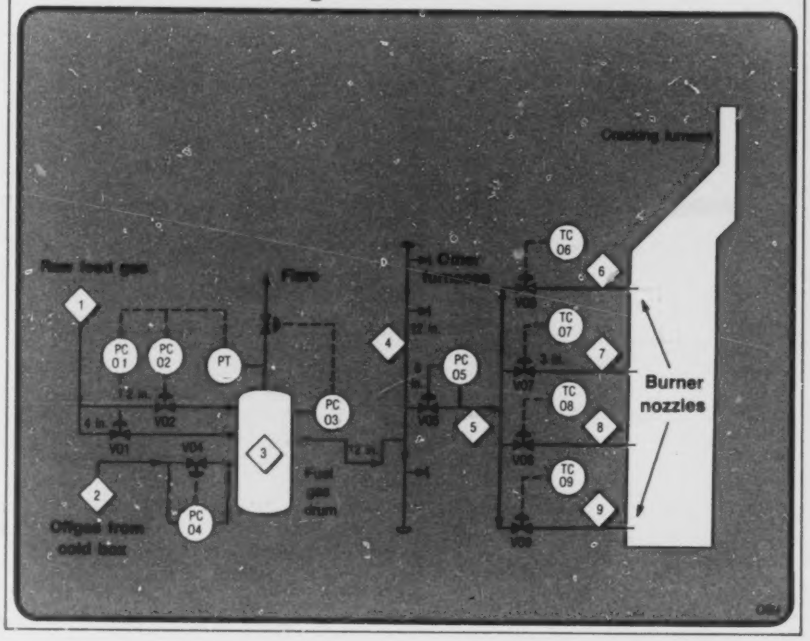
Most of the capital project support work has been done in-house. However, in some cases when the prime contractor has the capability for dynamic simulation, MRDC's role has been to review the models during their development and to assist in translating their results into action.

The major objective for most of the work in support of capital projects has been to verify/check the adequacy of the control systems which have been designed.

If dynamic simulation experiments indicate control or operational difficulties, then the dynamic models are used to develop solutions to these problems. Such changes are expected to be made prior to start-up; therefore, simulation engineers must work closely with the design engineers and must convince them of the validity of the models. Once this confidence has been established, the models are used to answer many other what-if questions, not all of which are limited to control system operations.

Fig. 1

Furnace fuel change P&ID



Facility-wide steam system models were developed for the New Zealand Synfuels plant,[1] and for another grass roots facility. In each case, these models were required because a relatively small number of steam turbines seemed likely to dominate the system's behavior. So, the models were used to study control system responses to trip/load rejection situations as well as to more gradual normal load changes.

These models included steam generation (fired boilers, waste heat generators), distribution headers and letdown stations, as well as major and minor steam turbines and their associated loads and controls.

All of these applications are characterized by the need for quite large, high fidelity models and by the long period over which they were used. Most of these dynamic models required between 100 and 400 differential equations and were developed and used intermittently over periods of 6 to 36 months. Although detailed validation of the models has not been obtained since plant start-up, continuing use of dynamic models and the absence of instances in which simulation-tested controls have proved inadequate indicate that results are generally accurate.

Mobil has used analog-computer-based training simulators for operator training in the use of plant controls since the start-up of the Joliet and Wilhelmshaven (Germany) refineries in the early 1970s. These simulations used relatively low-fidelity dynamic models, still based on proper mass and energy balances, both because of limited computing capability and because they were adequate for the training purposes.

By about 1980, new process facilities were being equipped with control systems using CRT-based operator display stations, and the cost of digital computers had fallen dramatically. Training simulators purchased since then have been digital-computer based and these have the computing capability to support higher fidelity models.

However, there is a strong relationship between model fidelity and cost. A plant-specific model having fidelity adequate for prestart-up training, but not for the refresher training of an experienced operator, might be expected to cost less than $80,000. Higher fidelity models which may deliver some of the benefits of a design quality dynamic simulation can cost several times that amount.

MRDC has done relatively little work in using dynamic simulation for the solution of control problems with operating plants. This is due both to the length of time needed to develop useful models and to a shortage of simulation engineers. Dynamic simulation studies did contribute to the resolution of initial operating problems with hydrocracker units in the early 1970s.

Fortunately, newer units have not experienced such severe control problems.

A significant amount of dynamic simulation work has been done in connection with de-bottlenecking and process revision studies for operating facilities. This category of work is seen as a major area of opportunity if better software tools can reduce the time needed to develop dynamic models.

**Simulation methodology.** A wide variety of tools has been used in dynamic simulations done on Mobil's behalf. All simulation models developed in-house have used IBM mainframe computer systems. But contractors and vendors have also used a variety of other systems (Table 2). It is not important which computer is used, as long as it has enough power to provide timely results and adequate display capabilities.

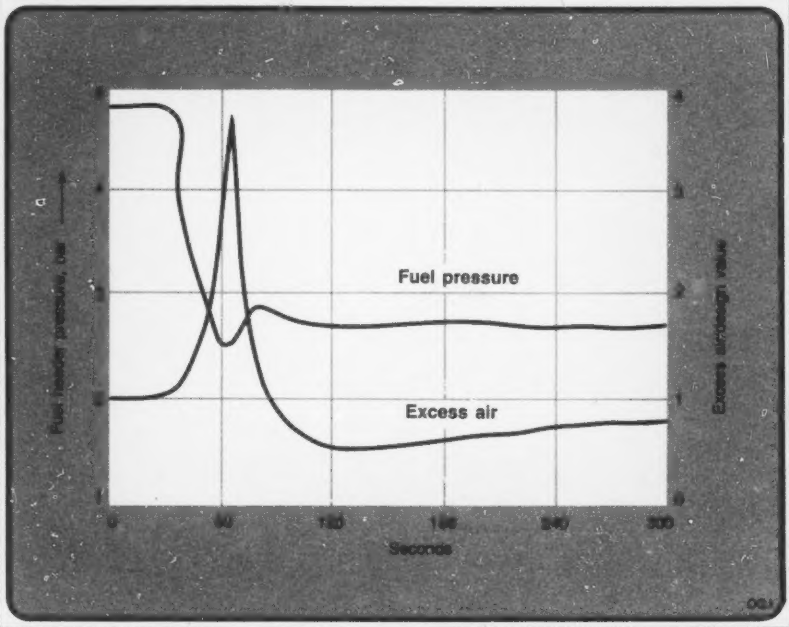
While Fortran is the dominant language that has been used, its current use is mostly as a vehicle for support of some higher level language.

CSMP (IBM) was an early example of such a higher level language, and used for MRDC's initial North Sea-related work. However, CSMP is essentially obsolete since support and maintenance are no longer available.

MRDC now uses Advanced Continuous Simulation language (ACSL) for its in-house work; this is a mature and reliable general purpose simulation language having good "hot-line" support and maintenance.[2] Also, it is available on many different computers. This tends to make models more portable.

Fig. 2

Actual fuel switch



DAP (Bechtel) is also a Fortran-based language and somewhat more process oriented than ACSL; it has been used successfully for several Mobil simulation studies.

GEPURS (Lummus/CE Simcon) is aimed at rapid development of training simulator quality models in an interactive and real-time environment. It is also Fortran based and has been used in both petrochemical and refinery applications.

Problems can arise during numerical integration. ACSL and even CSMP contain algorithms designed for use with such problems. However, the Euler method is used more often; its simplicity makes constraints easy to handle, and choice of a small enough stepsize is not hard.

Computer time savings, which might result from the use of more-sophisticated methods, are balanced by engineering time costs needed to specify error criteria separately for every integrator.

**Modeling techniques.** The first step in a new dynamic simulation is always an initial definition of scope. This is usually achieved by developing a simulation process and instrumentation diagram (P&ID) and a statement of the study objectives.

Model development then follows a divide-and-conquer strategy; the key idea is that the full model is built up by the interconnection of small models (modules) each of which represents one of the blocks/items from the simulation P&ID. Every component model/module is tested and proven on a stand-alone basis before inclusion in the complete model. This sharply reduces time spent in debugging.

Table 3 lists the two categories of modules currently available within MRDC for use in new simulation studies.

Although the re-use of existing modules provides a fast start, every project has enough special requirements that several new modules are needed. This situation should not change in the near future.

Development of new modules requires analysis based on the use of dynamic mass and energy balances; equipment mechanical and performance data, from vendors or from tests; and thermodynamic data and reaction kinetics information as needed. The equations used for any new module are strongly influenced by the assumptions made during its development.

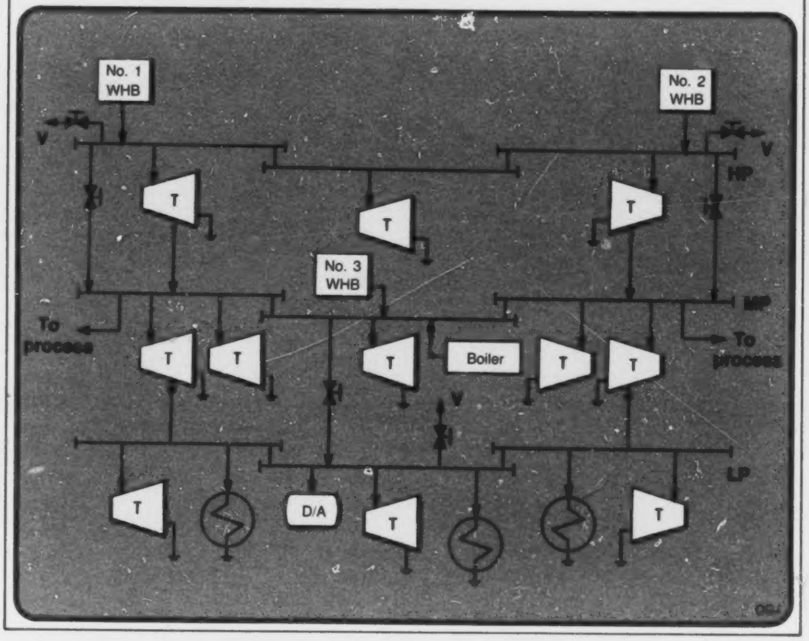
The techniques used for the development of lumped parameter models have been widely discussed.[3,4,5]

The level of detail included in any dynamic simulation model should be determined by the objectives of the study, because this has a major impact on the assumptions which can be made, and on the complexity and cost of the final model.

However, for capital project work using broad definitions of objectives, we have tended to make assumptions

Fig. 3

## Steam system simulation



## Equation nomenclature

| | |
|---|---|
| $A_i$ | Mass of air required to completely burn a unit mass of component i |
| LHV | Low heating value of fuel gas |
| $M_i$ | Mass hold-up of component i |
| MW | Average molecular weight of gas mixture |
| $MW_i$ | Molecular weight of component i |
| P | Absolute pressure |
| R | Ideal gas law constant |
| t | Time |
| T | Absolute temperature |
| V | Volume occupied by gas |
| $W_A$ | Combustion air mass flowrate |
| $W_F$ | Fuel gas mass flowrate |
| $W_{in}$ | Mass flowrate of the nth stream Feeding a node or gas volume |
| $W_0$ | Total mass flowrate leaving a node |
| $X_i$ | Mass fraction of component i at a node |
| $x_{in,i}$ | Mass fraction of component i in the $W_{in}$ stream |
| Z | Compressibility factor |

which require more rigor rather than less. This is based on the experience that fast answers will always be needed for what-if questions which we had not anticipated. A more rigorous model is more likely to be able to provide meaningful answers quickly.

Developing an accurate dynamic model is usually not the objective of a simulation study. More commonly, the model is used to assess the operability of a unit, the robustness of a proposed control scheme, or the safety of a system under abnormal operating conditions following a major upset. Therefore, communication among the various personnel involved is of major importance.

Table 4 lists the typical stages in the life cycle of a simulation study, and suggests the kind of interaction which is needed. Working relationships with process and facilities engineers can often be established by involving them in data collection, model validation, and development of a list of potential upsets.

Analysis of the results of simulation experiments is usually begun by the simulation engineers. But discussion of the results and of the conclusions drawn from them must involve other engineering disciplines if design or construction changes are actually going to be made.

A well-accepted dynamic model provides an excellent tool for the evaluation of alternative solutions to any problems which its use uncovers. However, the simulation engineers do not often develop the most practical solutions; input from process engineers, operations staff, etc., is essential.

The largest benefits are obtained from a dynamic simulation study when a team approach combines the efforts of those with process knowledge, mathematics and modeling skills, and engineering management authority. This way, the key findings of a simulation study are correct, are seen to be correct, and are implemented.

### Application examples

In normal operation, most of the fuel for an ethylene cracking furnace is provided by the hydrogen rich offgas stream from the cold box; this has a molecular weight of about 5. However, following a trip of the charge gas compressor, this fuel supply stops quickly.

In a recently designed gas-fed ethylene plant, the raw feed gas is used as furnace fuel after such a trip; it has a molecular weight of about 30.

The fuel gas burners could handle this big molecular weight change. But unless fuel gas pressure was reduced upstream of the burners a dangerous shortage of combustion air would occur in the firebox because the heavy fuel requires more air for complete combustion. The burner control system was designed to handle this situation. Because of the size of the fuel gas headers, the control system's performance was checked by dynamic simulation.

The simulation P&ID (Fig. 1) shows that all the available offgas flows into the fuel gas drum. The drum pressure is usually regulated by a controller (PC02) which manipulates a 2-in. control valve. Fuel gas flows through a long, 12-in. diameter supply pipe to a header which feeds several furnaces. There are four independent temperature control loops/furnace. Each loop controls firing rate by varying the fuel gas pressure at the burner spud.

If the offgas fuel supply is interrupted, the controller opens the valve fully. But this 2-in. valve has been carefully sized so that it cannot supply enough gas to maintain the controller's setpoint. The fuel gas pressure falls until a second controller (PC01), which has a lower pressure setpoint, opens a 4-in. fuel valve to balance supply and demand.

Process dynamic responses are described by a nine-capacity lumped parameter model (Nodes 1 through 9, Fig. 1). Pressure and composition of the fuel gas at each node are computed by six-component dynamic mass balances; fuel gas temperature effects are not important. The equations are (see box for definition of terms):

Mass balance/component.

$$dM_i/dt = \sum_n W_{in}\, x_{in,i} - W_0\, x_i \quad (1)$$

Mass fractions ($X_i$).

$$x_i = M_i / \sum_i M_i \quad (2)$$

Node pressure (P).

$$P = (ZRT/V) \sum_i (M_i/MW_i) \quad (3)$$

Controllers and control valves use standard models. The gas burner model, based on performance data

Table 1

## Mobil's applications

| Support of capital projects<br>Project/location | Subject |
|---|---|
| Arun field | Gas injection compressor system |
| Indonesia | LNG facility sub-systems, e.g. propane refrigeration loop |
| North Sea E&P facilities: Stratfjord A and Beryl A platforms | Gas/oil separation, gas handling, compressor systems, and injection wells |
| Petrochemical plant | Facility-wide steam system, ethylene unit sub-systems, Polyethylene unit sub-systems |
| New Zealand synfuels plant | Facility-wide steam system, methanol-to-gasoline unit |
| **Development of training simulators** | |
| Analog simulators | |
| Refineries: Joliet, Wilhelmshaven, etc. | Crude units(s), gas plant columns, boiler, fired heater, compressor, etc. |
| Digital simulators | |
| Yanbu Petrochemicals | Ethylene unit/ethylene oxide plant |
| New Zealand Synfuels | Steam system, MTG unit, basic training |
| **Support of operating facilities** | |
| U.S. hydrocracker | Multi-bed reactor and controls. |
| Refinery steam system | Effect of connecting HP headers |
| Offshore gas/oil production platforms | Re-wheeling in gas compression systems; sales gas and gas injection in parallel; interplatform transfer line studies |

Table 2

## Computers and software

| Computer systems | Application |
|---|---|
| EAI 690 hybrid | A run field injection compressor study |
| Autodynamics analog | Training simulators: Joliet, etc. |
| IBM 7094, 370/158, 3033, 3083,4361 (OS/MVS/CMS) | All simulation studies for which computer work was done by MRDC |
| Univac 1108; SEL 3200<br>PDP 11-23 and 44; SAGE IV | Used by contractors and/or system vendors |
| **Software** | |
| Fortran | As low level language to others |
| CSMP and CSMP III | Original CSSL packages; obsolete |
| ACSL | Used for new MRDC work, ACSL (1981) |
| DAP (Bechtel) | In-house package, Carlson (1982) |
| GEPURS (CE Simcon)<br>AUDYSIM (Autodynamics) | Both are in-house Fortran-based languages used for training simulator development. |
| **PASCAL** | |

Table 3

## Component models/ modules

**Generalized models: Packaged for immediate re-use**

| Model | Type/use |
|---|---|
| Controllers/control relays | Analog, not sampled data |
| Measuring transmitters | Measuring lags and scaling |
| Control valves (gas/liquid) | Include valve dynamics and choking |
| Flow resistance/pressure drop | For piping or equipment items |
| Gas phase capacity vessel | For one-component systems |
| Steam capacity node | Mixing of superheated streams |
| Multistage compressors | Centrifugal or reciprocating |
| Gas turbine | Two-shaft type |
| Steam turbine | Extraction; condensing; or small |
| Saturated steam generator | |
| **Specialized models: Not packaged for immediate re-use, expected to need modification** | |
| Multicomponent gas capacity | Mixing of superheated streams |
| Multicomponent flash/capacity | Mixing when two phases present |
| Fixed bed reactor(s) | Kinetics always different |
| Heat exchanger(s) | Counter-current, with and without phase changes; many variations possible |

from the vendor, calculates the fuel flow rate ($W_F$) from a power law function:

$$W_F = f(P, MW, LHV) \qquad (4)$$

Combustion air required ($W_A$)

$$W_A = \sum_i W_F \times F_i A_i \qquad (5)$$

The low heating value (LHV) is calculated from handbook data, given the fuel composition ($X_{Fi}$), as are the $A_i$ coefficients, for air required for complete combustion/lb of component i.

These equations model the fuel gas system and can compute the fuel flow rate, pressure, and composition changes which follow a compressor trip. Note that furnace temperatures are not modeled at all since this would greatly complicate the model without altering its conclusions.

The first model runs assumed that the furnace temperature controllers, TC06, etc., were in manual mode, so the valve settings do not change. Later runs assumed that these valves were driven open as fast as possible. It was further assumed that the air supply to the burners remains constant.

Off-line calculations of furnace draft were then made, using the computed fuel flow rates to obtain temperature profiles; on this basis, the constant combustion air flow assumption was validated.

Initial simulation results showed satisfactory control system responses, given a good choice for the setpoint and loop tuning constants of controller PC01. The model established these good choice values. The model was then used for a number of parameter sensitivity runs to test that performance remained good with fewer furnaces on-line, and in spite of different control loop tuning and control valve dynamic responses.

Fig. 2 shows one of these system responses; note that excess combustion air, the key variable, initially rises, as the offgas fuel flow decreases, then overshoots to a minimum value before settling to a lower-than-initial steady value. These results were judged to be acceptable after review by furnace and operations specialists. Best of all, the control scheme has been shown to work properly in the plant. The compressor did trip, and the furnace remained on line with only minor upset.

**Steam system study.** An example of a more typical design phase dynamic simulation study is the work done on the steam system of the synthetic fuels facility now being built in New Zealand. Fig. 3 is a very simplified sketch of this system; there are three steam headers, each at a different pressure; there are five major steam turbines, driving compressors, and about 12 smaller turbines. The two HP steam generators, each having three steam drums, are actually waste heat boilers in the exhaust duct of the two methanol reformer furnaces.

The control system model includes about 40 loops. The full dynamic model has somewhat over 400 differential equations.

A dynamic model for this steam system was developed quite early in the design stage of the project. It was used to simulate the effect of a number of major trips and equipment failures, and was archived after those results had been fully evaluated.

Midway through the construction phase of the project, the model was updated, since there had been many minor changes over a 2-year period. It was then used to answer several new what-if questions.

The results obtained led to some significant changes in the control system; and to the establishment of rational and practical load shedding strategies for use after a trip of one steam generator. They were also used in the development of a special training simulator program for the steam system.

**Ethylene vaporizaton system.** A simulation was also made of the ethylene vaporization system in a Saudi Arabian petrochemical complex.[6] The primary objective of this simulation was to design and evaluate a control plan and evaluate the system's operating procedures.

The system provides an adequate, uninterrupted supply of ethylene to two downstream derivative units when the main ethylene supply is lost. The simulation included the vaporizer system and the tail end of the ethylene unit. The major pieces of equipment represented in the simulation model were the ethylene vaporizers, heat exchangers, pumps, and storage tanks. In the process, ethylene from the ethylene fractionator is collected in the ethylene product drum. During normal operation, most of this ethylene is supplied to the downstream users. Some is chilled and stored. If one or both of the users are shut down, this unused ethylene is also stored.

Liquid ethylene is stored in two tanks, each with a working capacity of 16,900 tons. During an ethylene unit shutdown, liquid ethylene is pumped from storage, vaporized in an indirect shell-and-tube-type heat exchanger, and transferred to the ethylene distribution header. Based on various operating situations, the control system was required to:

- Maintain the pressure in the ethylene distribution header within 2% of 3,384 kPa(g) during normal operation, without using the vaporizer.
- Maintain the pressure in the ethylene distribution header above 2,900 kPa(g) during an ethylene unit shutdown with all ethylene users operating at full capacity.
- Maintain the pressure in the ethylene distribution header within 2% of 3,384 kPa(g) during partial capacity operation of the ethylene unit with all ethylene users operating at full capacity.
- Maintain the header pressure within 2% of 3,384 kPa(g) during normal operation of the ethylene unit and with one or more of the using units operating at partial capacity.
- Maintain the pressure in the ethylene vaporizer tubes above critical.
- Maintain a specified minimum level in the product vaporizer.
- Provide for minimum operator input during abnormal operation, i.e., start-up, shutdown, and product flaring.

Two control systems were developed. One comprised a combination of feedforward and feedback schemes.

**Simulation implementation.** The mathematical model was divided into five individual modules which were interconnected to simulate the variations and interactions of pressures and flows. The major modules were models of the flow network, vaporizer, reboiler, heat exchanger, and pump.

A dynamic analysis program developed by Bechtel was used to generate the computer simulation. Models for individual process units were tested on an individual basis, then integrated to form a working simulation model.

This simulation model was used to form the various steady states required for the simulation runs: vaporizer standby, ethylene shutdown, partial capacity, and flaring. The latter steady states were derived from the vaporizer standby condition after successfully tuning the basic controllers. The valve stroke times and characteristics were adjusted as required.

A series of planned upsets was used to evaluate the performance of the control systems. As a result, the control system including feedforward and feedback components was found capable of activating and controlling the vaporization system and the other process sections to meet all the outlined criteria, without any modification of the equipment as designed. The other system would have required costly design modifications to achieve the same control. It was also much slower in response.

**Future developments.** A major weakness of dynamic process simulation is that it is expensive and time consuming; thus, its use tends to be restricted to major projects or problems.

However, the cost of raw computation continues to fall rapidly. It is obvious that we should look for better software to use this lower cost of computation to reduce simulation expense. There have been a number of attempts in this direction, but versatile and flexible process dynamic simulation packages are still not available.

The key features of such a package would include:

- A user-friendly interface so that the "new user entry fee" would be small enough to permit process or control engineers to play a significant part in future dynamic simulation studies.
- The availability of many simple models so that "first cut" dynamic analysis can contribute to process feasibility studies.
- The ability to have "expert users" extend the system by addition of other component models on a temporary or permanent basis.
- A data transfer interface to steady state process-simulation packages so that stream specifications and physical property data can be used more quickly and reliably.

A successful package would permit exploitation of the 80/20 rule. The packaged models could be expected to accomplish 80% of the work very quickly, freeing the simulation specialist to confront the 20% which could not be handled by the packaged models.

MRDC has begun development of a package having some of these features, with the objective of making at least all of the generalized component models easily available for use by nonspecialists. We regard ACSL as an effective general purpose simulation language, and are grafting process simulation features onto it by providing a special user interface.

The user defines the scope of his dynamic model by preparing a simulation P&ID and by collecting the data needed to define the physical system. He is then "interviewed" by a custom-written (dBase III) program, which runs on an IBM PC/AT. This

Table 4

## Work phases

| Stage | Requires interaction with ... |
|---|---|
| Problem definition | Project management; process, control, equipment, and operations engineers |
| Formulate equations and math model | Process, control, and equipment engineers |
| Collect data | Process, control, and equipment engineers |
| Build and validate model | Process, control, and equipment engineers |
| Report on plan and model definition: | Project management; process, control, equipment, and operations engineers |
| Discuss with users | |
| Execute planned experiments | Process, control, and equipment engineers |
| Resolve problems which have been identified | Project management; process, control, equipment, and operations engineers |
| Additional work to resolve "what-if" questions | Process, control, equipment, and operations engineers |
| Final report and archive model | |

program organizes the data and system inter-connection information from the P&ID, and a skeleton of a run-time-data file which is needed to execute experiments with the ACSL model. Thus, if the physical system can be modeled entirely with components included in the PC's program generator, the user need know nothing about the syntax of ACSL. The PC-generated files are transferred to a mainframe computer for execution, although this may be done on the PC for small models.

MRDC experience has been that no dynamic simulation study has been completed without the development of some special component models. This requirement will be handled in two ways. First, the PC's program generator software system can be modified to include additional component models, by means of another interview process with an "expert user." Alternatively, the simulation engineer can modify the PC-generated ACSL program before it is translated, adding a code to represent the special features of the physical system for which standardized models do not exist or are not adequate.

**Conclusions.** The value of dynamic simulation is well established. Benefits flow from better understanding of systems, from the reduction of unexpected control loop interactions, and from better control. We strive to reduce the "opinion engineering" content of plant design and to provide twenty-twenty hindsight before start up, a form of twenty-twenty foresight.

The major factor limiting the use of dynamic simulation seems to be that it is too difficult. This makes it an expensive and slow-to-use tool. Better software systems and faster/cheaper computers will help. Perhaps the use of parallel-processor computers will cause a major change.

However, experience suggests that today's target ought to be to provide general tools which can quickly solve 80% of the typical problem and which permit the simulation engineer's expertise to add the last 20%. Our work with the PC program generator system has this objective. Still, dynamic simulation will likely remain a specialist activity. It has a uniquely broad range of involvement across many discipline lines in any major project.

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# Program for microcomputers estimates air-cooled heat-exchanger design data

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Design data for air-cooled heat exchangers in gas, liquid, and partial and complete condensing services can be estimated by a program developed for personal computers. These data can be used for the preliminary design of an exchanger.

The program will calculate the log-mean-temperature difference (LMTD), the number of tube rows, the estimated fan power required, the bare-tube surface area required, the face area required, and the estimated total weight of the exchanger.

Typical heat-transfer coefficents for the various services are provided by the program. However, the program is arranged so that coefficients calculated or determined from other means may be used.

The algorithm and basic equations for the program are given, and examples of the program's use are presented for gas, liquid, and condensing services.

The program is designed to run on an Apple IIe personal computer with 128K RAM. It can also be easily modified or converted for use with other microcomputers.

**Air cooling.** Ambient air has been used to cool process fluids in air-cooled heat exchangers for many years. Air-cooled heat exchangers are particularly popular where cooling water is scarce.

Many articles on the design and specifications of air-cooled exchangers have been published. Some deal with the design procedures, specifications, and calculations of heat-transfer coefficients. Others deal with the mechanical features of finned-tube elements, tube bundles, fans and fan motors, forced draft vs. induced draft, and temperature control.

## Nomenclature

| | |
|---|---|
| A | Surface area based on tube OD, sq ft |
| FA1 | Face area of tube bundle via Eq. 2, sq ft |
| FA2 | Face area of tube bundle via (A/R), sq ft |
| G | Unit weight per square foot face area, lb/sq ft |
| $h_a$ | Air-side film heat-transfer coefficient, BTU/hr-sq ft °F. |
| $h_i$ | Inside film heat transfer coefficient, BTU/hr-sq ft °F. |
| LMTD | Effective log mean temperature difference, °F. |
| P | Bare tube surface area per horsepower, sq ft/hp |
| Q | Total heat duty, BTU/hr |
| R | Square feet surface area per square foot face area, sq ft/sq ft |
| $R_{if}$ | Fouling resistance of process fluids inside tube, (BTU/hr-sq ft °F.)$^{-1}$ |
| $R_m$ | Resistance of tube metal, (BTU/hr-sq ft °F.)$^{-1}$ |
| $T_1$ | Process fluid inlet temperature, °F. |
| $T_2$ | Process fluid outlet temperature, °F. |
| $T_3$ | Ambient air temperature, °F. |
| $T_4$ | Air outlet, temperature, °F. |
| U | Overall heat transfer coefficient (based on bare tube OD), BTU/hr-sq ft °F. |
| V | Face velocity of air, scfm |

Although step-by-step procedures for the preliminary design of air cooled exchangers have been presented,[1] [4] these procedures frequently involve tedious trial-and-error calculations.

The trial-and-error calculations lend themselves well to the application of microcomputer programs.

Cooling services may be simple gas cooling, or liquid cooling. They may also involve more complicated partial condensation or total condensation services.

Overall heat transfer coefficients can be calculated by more rigorous methods.[5] [9] But, some typical coefficients for various services encountered in chemical, oil, and gas processing plants may be sufficient for the preliminary sizing of air coolers.

In addition, the preliminary horsepower consumption by the air coolers is frequently needed in order to determine the overall plant electrical, steam, and other utility requirements. The exchanger surface areas, face areas, and the estimated weight are also needed for plot-plan development and layout of foundations. A microcomputer program capable of providing this information can certainly expedite the progress of a chemical, gas, or oil processing facility design and construction project.

The algorithm for the program is shown in Fig. 1. The complete program listing is shown in Fig. 2.

Input data required for the program include: the process fluid inlet temperature, T1; the process fluid outlet temperature, T2; the ambient air temperature, T3; and the total cooling duty, Q.

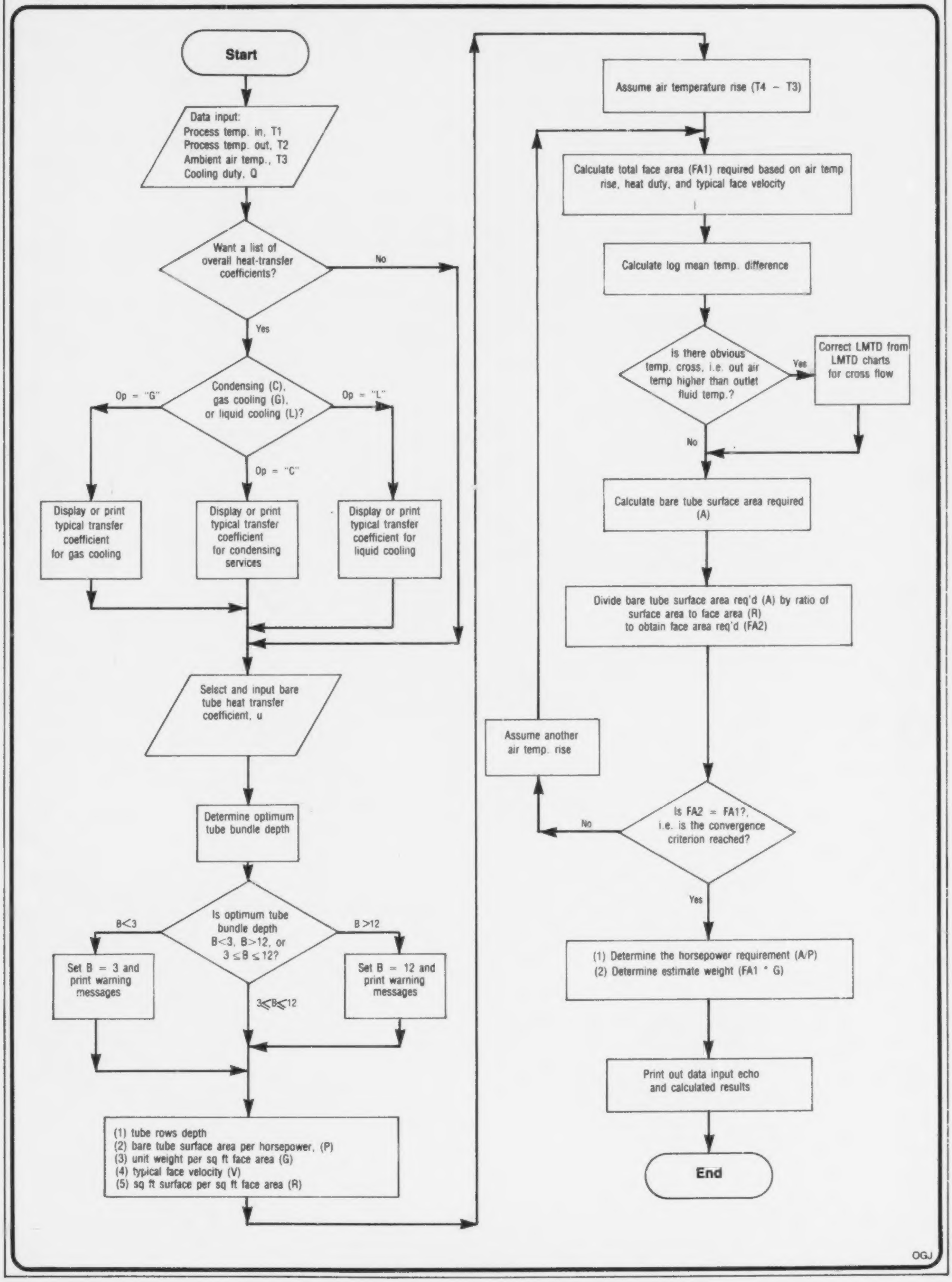
**Heat-transfer coefficients.** After the input data are keyed in, the computer will ask the question whether the user wants a list of typical overall heat transfer coefficients, U. If the answer is yes, the computer will then ask whether the user wants the overall transfer coefficient for simple gas cooling (G), simple liquid (L), or condensation cooling (C).

Depending on the answer (G, L, or C), the computer will display the typical overall heat transfer coefficients on the screen for the user to select. The typical overall heat transfer coefficients for air-cooler services encountered in chemical, oil, and gas processing are shown (Figs. 3, 4, and 5) for gas cooling, liquid cooling, and condensing cooling. These coefficients are compiled from a number of sources in the literature.[1] [3] [4] [5]

If the answer for displaying the overall heat transfer coefficients is no, the user is then prompted to input the heat-transfer coefficients. The heat-transfer coefficients can be calculated via rigorous methods such as equa-

Fig. 1

## Algorithm of air-cooled heat exchanger program



Start
Data input:
Process temp. in, T1
Process temp. out, T2
Ambient air temp., T3
Cooling duty, Q
Want a list of overall heat-transfer coefficients?
No
Yes
Condensing (C), gas cooling (G), or liquid cooling (L)?
Op = "G"
Op = "L"
Op = "C"
Display or print typical transfer coefficient for gas cooling
Display or print typical transfer coefficient for condensing services
Display or print typical transfer coefficient for liquid cooling
Select and input bare tube heat transfer coefficient, u
Determine optimum tube bundle depth
Is optimum tube bundle depth B<3, B>12, or 3 ≤ B ≤ 12?
B<3
B >12
3≤B≤12
Set B = 3 and print warning messages
Set B = 12 and print warning messages
(1) tube rows depth
(2) bare tube surface area per horsepower, (P)
(3) unit weight per sq ft face area (G)
(4) typical face velocity (V)
(5) sq ft surface per sq ft face area (R)
Assume air temperature rise (T4 – T3)
Calculate total face area (FA1) required based on air temp rise, heat duty, and typical face velocity
Calculate log mean temp. difference
Is there obvious temp. cross, i.e. out air temp higher than outlet fluid temp.?
Yes
Correct LMTD from LMTD charts for cross flow
No
Calculate bare tube surface area required (A)
Divide bare tube surface area req'd (A) by ratio of surface area to face area (R) to obtain face area req'd (FA2)
Assume another air temp. rise
No
Is FA2 = FA1?, i.e. is the convergence criterion reached?
Yes
(1) Determine the horsepower requirement (A/P)
(2) Determine estimate weight (FA1 * G)
Print out data input echo and calculated results
End

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```
10  REM     THIS IS A PROGRAM FOR AIR-COOLED HEAT EXCHANGER ESTIMATE AND PRELIMINARY DESIGN.
20  REM  THE PROGRAM WAS CREATED BY DR. TOM C. TSAI.
50  DEF  FN P(X) =  INT (1E2 * (X + 0.005)) / 1E2
60  HOME
80  INPUT "ENTER THE EXCHANGER EQUIPMENT NUMBER ";E$
90  REM  LEN IS THE VARIABLE FOR LENGTH OF STRING.
100  IF  LEN (E$) <  = 10 THEN 130
110  PRINT "EQUIPMENT NUMBER MUST BE 10 CHARACTERS OR LESS."
120  GOTO 80
130  PRINT
140  PRINT "ENTER THE FOLLOWING VALUES (ALL TEMPS ARE IN DEGREE F): "
150  PRINT
160  INPUT "PROCESS TEMPERATURE IN, DEG-F : ";T1
170  INPUT "PROCESS TEMPERATURE OUT,DEG-F : ";T2
180  INPUT "AMBIENT AIR TEMPERATURE,DEG-F : ";T3
190  INPUT "COOLING DUTY, MMBTU/HR        : ";Q
200 Q = Q * 1000000.0: PRINT
210  INPUT "WOULD YOU LIKE A LIST OF TYPICAL OVERALL HEAT TRANSFER COEFFICIENT?(Y/N) : ";A$
220  IF A$ = "N" THEN 1830
230  IF A$ = "Y" THEN 250
240  GOTO 210
250  PRINT : INPUT "IS THE SERVICE CONDENSING,GAS COOLING OR LIQUID COOLING?(ENTER C,G OR L) :";B$
260 M = 0
270  IF B$ = "C" THEN M = 1
280  IF B$ = "G" THEN M = 2
290  IF B$ = "L" THEN M = 3
300  IF M = 0 THEN 250
310  PRINT : PRINT
320  REM  SOURCES OF THE TYPICAL HEAT TRANSFER COEFFICIENTS ARE AS FOLLOWS:
330  REM  E.C.SMITH, "AIR COOLED HEAT EXCHANGERS-A NEW INDUSTRIAL COOLING MEDIUM
340  REM  FOR COOLING PROCESS STREAMS IN OIL, GAS, AND CHEMICAL PLANTS."
350  REM  J.E.LERNER,SIMPLIFIED AIR COOLER ESTIMATING,HYDROCARBON PROCESSING
360  REM  FEBRUARY, 93-100 (1972).
370  REM  AIR COOLED HEAT EXCHANGE, CHEM. ENG. PROG. VOL.55, NO.4, APRIL, 1959.
380  REM  F.AERSTIN AND G. STREET,"APPLIED CHEMICAL PROCESS DESIGN," PLENUM PRESS, NEW YORK, 1978.
390  REM  "BASICS OF AIR COOLED HEAT EXCHANGERS," BROCHURES OF HUDSON PRODUCTS CORP., HOUSTON, TEXAS.
400  INPUT "DO YOU WANT A HARDCOPY PRINTOUT? (Y/N) ";HC$
410  IF HC$ = "N" THEN 450
420  IF HC$ = "Y" THEN 430
430  PRINT  CHR$ (4);"PR#1": REM  ACTIVATE PRINTER
440  PRINT  CHR$ (9);"132N": REM  DEACTIVATE SCREEN
450  PRINT " TYPICAL HEAT TRANSFER COEFFICIENTS FOR AIR-COOLED HEAT EXCHANGER: "
460  PRINT
470  PRINT "------------------------------------------------------------------------"
480  ON M GOTO 490,1110,1470
490  PRINT "CONDENSING";
500  POKE 36,55: PRINT "BARE TUBE U"
510  PRINT " SERVICE";
520  POKE 36,55: PRINT "(BTU/HR-SQ.FT-DEG F)"
530  PRINT "------------------------------------------------------------------------"
540  PRINT "TOTAL CONDENSER:"
550  PRINT "AMINE REACTIVATOR";
560  POKE 36,55: PRINT "90-100"
570  PRINT "AMMONIA";
580  POKE 36,55: PRINT "100-120"
590  PRINT "FREON 12";
600  POKE 36,55: PRINT "60-80"
610  PRINT "HEAVY NAPHTHA";
620  POKE 36,55: PRINT "60-70"
630  PRINT "KEROSENE";
640  POKE 36,55: PRINT "65"
650  PRINT "LIGHT GASOLINE";
660  POKE 36,55: PRINT "80"
670  PRINT "LIGHT HYDROCARBONS";
680  POKE 36,55: PRINT "80-95"
690  PRINT "LIGHT NAPHTHA";
700  POKE 36,55: PRINT "70-80"
710  PRINT "PENTANES THRU LIGHT NAPHTHA, 70 PSIG";
720  POKE 36,55: PRINT "90"
730  HTAB 30: PRINT "20 PSIG";
740  POKE 36,55: PRINT "85"
750  HTAB 30: PRINT "10 PSIG";
760  POKE 36,55: PRINT "75"
770  PRINT "REACTOR EFFLUENT-PLATFORMERS,REXFORMERS,HYDROFORMERS";
780  POKE 36,55: PRINT "60-80"
790  PRINT "STEAM (0-20 PSIG)";
800  POKE 36,55: PRINT "130-140"
810  PRINT "STILL OVHD-LIGHT NAPHTHAS,STEAM & NON-CONDENSABLE GAS";
820  POKE 36,55: PRINT "60-70"
830  IF HC$ = "N" THEN 870
840  IF H[illegible] = "Y" THEN 850
850  PRINT  CHR$ (9);"I": REM   REACTIVATE SCREEN
860  PRINT  CHR$ (4);"PR#0": REM  DEACTIVATE PRINTER
870  INPUT "PRESS RETURN KEY TO CONTINUE ";CO$
880  IF HC$ = "N" THEN 920
890  IF HC$ = "Y" THEN 900
900  PRINT  CHR$ (4);"PR#1": REM  ACTIVATE PRINTER-
910  PRINT  CHR$ (9);"132N": REM  DEACTIVATE SCREEN
920  PRINT "PARTIAL CONDENSER:"
930  PRINT "HYDROGEN-RICH REACTOR EFFLUENT"
940  PRINT "  HYDROCRACKER,1400-3000 PSIG";
950  POKE 36,55: PRINT "80"
960  PRINT "  CAT.REFORMER,350-450 PSIG";
970  POKE 36,55: PRINT "75"
980  PRINT "  HYDROTREATERS,NAPHTHA";
990  POKE 36,55: PRINT "70"
1000  PRINT "  HYDROTREATERS,GAS OIL";
1010  POKE 36,55: PRINT "60-70"
1020  PRINT "CRUDE COLUMN OR STABILIZER OVHD";
1030  POKE 36,55: PRINT "65"
1040  PRINT "CAT.CRACKER FRACTIONATOR OVHD";
1050  POKE 36,55: PRINT "75"
1060  PRINT "------------------------------------------------------------------------"
1070  PRINT  CHR$ (9);"I": REM  REACTIVATE SCREEN
1080  PRINT  CHR$ (4);"PR#0": REM  DEACTIVATE PRINTER
1090  INPUT "PRESS RETURN KEY TO CONTINUE     ";CC$
1100  GOTO 1800
1110  PRINT "GAS COOLING";
1120  POKE 36,55: PRINT "BARE TUBE U"
1130  PRINT "SERVICE";
1140  POKE 36,55: PRINT "(BTU/HR-SQ.FT-DEG F)"
1150  PRINT "------------------------------------------------------------------------"
1160  PRINT "AIR OR FLUE GAS :"
1170  PRINT "  @50 PSIG (DELTA P = 1 PSI)";
1180  POKE 36,55: PRINT "10"
1190  PRINT "  @100 PSIG (DELTA P = 2 PSI)";
1200  POKE 36,55: PRINT "20"
1210  PRINT "  @100 PSIG + (DELTA P = 5 PSI)";
1220  POKE 36,55: PRINT "30"
1230  PRINT "AMMONIA REACTOR STREAM";
1240  POKE 36,55: PRINT "80-90"
1250  PRINT "ETHYLENE";
1260  POKE 36,55: PRINT "80"
1270  PRINT "HYDROGEN,250 PSIG (DELTA P=3 PSI)";
1280  POKE 36,55: PRINT "60"
1290  PRINT "HYDROCARBON GASES:"
1300  PRINT "  @15-50 PSIG (DELTA P = 1 PSI)";
1310  POKE 36,55: PRINT "30-40"
1320  PRINT "  @50-250 PSIG (DELTA P = 3 PSI)";
1330  POKE 36,55: PRINT "50-60"
1340  PRINT "  @250-1500 PSIG (DELTA P = 5 PSI)";
1350  POKE 36,55: PRINT "70-90"
1360  PRINT "NATURAL GAS,0-50 PSIG (DELTA P=1 PSI";
1370  POKE 36,55: PRINT "35"
1380  HTAB 13: PRINT "50-200 PSIG (DELTA P=3 PSI)";
1390  POKE 36,55: PRINT "50"
1400  HTAB 13: PRINT "200-1500 PSIG (DELTA P=1 TO 10 PSI)";
1410  POKE 36,55: PRINT "60-95"
1420  PRINT "------------------------------------------------------------------------"
1430  PRINT  CHR$ (9);"I": REM  REACTIVATE SCREEN
1440  PRINT  CHR$ (4);"PR#0": REM  DEACTIVATE PRINTER
1450  INPUT "PRESS RETURN KEY TO CONTINUE     ";GG$
1460  GOTO 1800
1470  PRINT "LIQUID COOLING";
1480  POKE 36,55: PRINT "BARE TUBE U"
1490  PRINT "  SERVICE";
1500  POKE 36,55: PRINT "(BTU/HR-SQ.FT-DEG F)"
1510  PRINT "------------------------------------------------------------------------"
1520  PRINT "ENGINE JACKET WATER";
1530  POKE 36,55: PRINT "120-130"
1540  PRINT "FUEL OIL";
1550  POKE 36,55: PRINT "20-30"
1560  PRINT "LEAN CARBONATE SOLUTION";
1570  POKE 36,55: PRINT "80"
1580  PRINT "LEAN AMINE, 15-20 WT.%";
1590  POKE 36,55: PRINT "100"
1600  HTAB 13: PRINT "20-25 WT.%";
1610  POKE 36,55: PRINT "95"
1620  PRINT "LIGHT GAS OIL";
1630  POKE 36,55: PRINT "60-70"
1640  PRINT "LIGHT HYDROCARBONS";
1650  POKE 36,55: PRINT "75-95"
1660  PRINT "LIGHT NAPHTHA";
1670  POKE 36,55: PRINT "70"
1680  PRINT "PROCESS WATER";
1690  POKE 36,55: PRINT "105-120"
1700  PRINT "RESIDUUM";
1710  POKE 36,55: PRINT "10-20"
1720  PRINT "SULFINOL, 7 CP. OUTLET";
1730  POKE 36,55: PRINT "70"
1740  PRINT "TAR";
1750  POKE 36,55: PRINT "5-10"
1760  PRINT "------------------------------------------------------------------"
1770  PRINT  CHR$ (9);"I": REM  REACTIVATE SCREEN
1780  PRINT  CHR$ (4);"PR#0": REM  DEACTIVATE PRINTER
1790  INPUT "PRESS RETURN KEY TO CONTINUE     ";LL$
1800  HOME
1810  REM  BEEP
1820  PRINT  CHR$ (7)
1830  PRINT : INPUT "ENTER BARE TUBE TRANSFER COEFFICIENT (BTU/HR-SQ.FT-DEG F) : ";U
1840  REM  THIS IS THE BUNDLE DEPTH ROUTINE.
1850 X = (T1 - T3) / U
1860 B = 3.041 + 3.899 *  LOG (X)
1870 B =  INT (B + 0.5)
1880  IF B >  = 3 AND B <  = 12 THEN 1900
1890  PRINT
1900  PRINT "THE CALCULATED TUBE BUNDLE DEPTH IS OUTSIDE THE RANGE OF PROCEDURE"
1910  IF B > 12 THEN 1950
1920 B = 3
1930  PRINT "THE TUBE BUNDLE DEPTH HAS BEEN SET TO THE MINIMUM VALUE OF 3"
1940  GOTO 1970
1950 B = 12
1960  PRINT "THE TUBE BUNDLE DEPTH HAS BEEN SET TO THE MAXIMUM VALUE OF 12"
1970  PRINT : PRINT : PRINT : PRINT
1980  FOR I = 1 TO B - 2
1990  READ P,G,V,R
2000  NEXT I
```

```
2010 Y = 0
2020 T4 = T3 + 10
2030 A2 = Q / ((T4 - T3) * V * 1.08)
2040 GOSUB 2190
2050 A1 = Q / (U * D1)
2060 F1 = A2 - A1 / R
2070  IF F1 = 0 THEN 2390
2080  IF Y = 1 THEN 2120
2090 Y = 1:T5 = T4
2100 T4 = T4 + 10
2110 F2 = F1: GOTO 2030
2120  IF  ABS ((F1 - F2) / F1) < 5E - 03 THEN 2390
2130 F3 = F1 - F2
2140 T6 = F1 / (F3 / (T4 - T5))
2150 T5 = T4
2160 T4 = T4 - T6
2170 F2 = F1
2180  GOTO 2030
2190  REM  THIS IS THE LMTD SUBROUTINE.
2200 T7 = T1 - T4
2210 T8 = T2 - T3
2220  IF T7 > T8 THEN 2260
2230 T9 = T7
2240 T7 = T8
2250 T8 = T9
2260 D1 = (T7 - T8) /  LOG (T7 / T8)
2270  RETURN
2280  REM  THIS IS THE TUBE BUNDLE DATA.
2290  DATA  48,66,630,3.8
2300  DATA  59,75,595,5.04
2310  DATA  69,80,565,6.32
2320  DATA  80,88,540,7.6
2330  DATA  91,97,510,8.84
2340  DATA  103,115,490,10.08
2350  DATA  116,126,465,11.36
2360  DATA  129,131,445,12.64
2370  DATA  134,140,425,13.92
2380  DATA  152,147,405,15.2
2390  PRINT  CHR$ (23)
2400  IF HC$ = "N" THEN 2490
2410  IF HC$ = "Y" THEN 2470
2420  IF A$ = "Y" THEN 2470
2430  IF A$ = "N" THEN 2440
2440  INPUT "DO YOU WANT TO OBTAIN A HARDCOPY FOR RESULTS? (Y/N) : ";RC$
2450  IF RC$ = "N" THEN 2490
2460  IF RC$ = "Y" THEN 2470
2470  PRINT  CHR$ (4);"PR#1": REM  ACTIVATE PRINTER
2480  PRINT  CHR$ (9);"132N": REM  DEACTIVATE SCREEN
2490  PRINT "THE RESULTS ARE : ": PRINT
2500  PRINT "*********************************  ****************************************"
2510  PRINT : PRINT "AIR-COOLED EXCHANGER NO.: ";
2520  POKE 36,55: PRINT E$
2530  PRINT : PRINT "------------------------------------------------------------------------"
2540  PRINT
2550  PRINT "  PROCESS TEMP., DEG-F:";
2560  POKE 36,40: PRINT "IN";
2570  POKE 36,55: PRINT  FN P(T1)
2580  POKE 36,40: PRINT "OUT";
2590  POKE 36,55: PRINT  FN P(T2)
2600  PRINT "  AIR TEMP., DEG-F:";
2610  POKE 36,40: PRINT "IN";
2620  POKE 36,55: PRINT  FN P(T3)
2630  POKE 36,40: PRINT "OUT";
2640  POKE 36,55: PRINT  FN P(T4)
2650  PRINT "  HEAT TRANSFER DUTY, MMBTU/HR:";
2660  POKE 36,55: PRINT  FN P(Q / 1000000.0)
2670  PRINT
2680  PRINT "  LOG MEAN DELTA TEMP., DEG-F: ";
2690  POKE 36,55: PRINT  FN P(D1)
2700  PRINT "  OVERALL TRANSFER COEFF. U, BTU/HR-SQ.FT-DEG F: ";
2710  POKE 36,55: PRINT  FN P(U)
2720  PRINT "  TUBE ROWS:";
2730  POKE 36,55: PRINT B
2740  PRINT "  ESTIMATED FAN POWER, HP:";
2750  POKE 36,55: PRINT  FN P(A1 / P)
2760  PRINT "  EST. BARE TUBE SURFACE AREA, SQ.FT:";
2770  POKE 36,55: PRINT  FN P(A1)
2780  PRINT "  ESTIMATED FACE AREA, SQ.FT:";
2790  POKE 36,55: PRINT  FN P(A2)
2800  PRINT "  ESTIMATED WEIGHT, LBS.:";
2810  POKE 36,55: PRINT  FN P(A2 * 6)
2820  PRINT
2830  PRINT "**************************************************************************"
2840  IF HC$ = "N" THEN 2880
2850  IF HC$ = "Y" THEN 2860
2860  PRINT  CHR$ (9);"I": REM  REACTIVATE SCREEN
2870  PRINT  CHR$ (4);"PR#0": REM  DEACTIVATE PRINTER
2880  END
```

**Air cooled** heat exchanger design program (Fig. 2).

```
 TYPICAL HEAT TRANSFER COEFFICIENTS FOR AIR-COOLED HEAT EXCHANGER:

--------------------------------------------------------------------------
GAS COOLING                                                 BARE TUBE U
SERVICE                                                     (BTU/HR-SQ.FT-DEG F)
--------------------------------------------------------------------------
AIR OR FLUE GAS :
  @50 PSIG (DELTA P = 1 PSI)                                10
  @100 PSIG (DELTA P = 2 PSI)                               20
  @100 PSIG + (DELTA P = 5 PSI)                             30
AMMONIA REACTOR STREAM                                      80-90
ETHYLENE                                                    80
HYDROGEN,250 PSIG (DELTA P=3 PSI)                           60
HYDROCARBON GASES:
  @15-50 PSIG (DELTA P = 1 PSI)                             30-40
  @50-250 PSIG (DELTA P = 3 PSI)                            50-60
  @250-1500 PSIG (DELTA P = 5 PSI)                          70-90
NATURAL GAS,0-50 PSIG (DELTA P=1 PSI                        35
          50-200 PSIG (DELTA P=3 PSI)                       50
          300-1500 PSIG (DELTA P=1 TO 10 PSI)               60-95
--------------------------------------------------------------------------


THE RESULTS ARE :

**************************************************************************

AIR-COOLED EXCHANGER NO.:                                   E-305

----------------------  --------------------------------------------------

  PROCESS TEMP., DEG-F:                     IN              350
                                            OUT             200
  AIR TEMP., DEG-F:                         IN              90
                                            OUT             234.7
  HEAT TRANSFER DUTY, MMBTU/HR:                             250

  LOG MEAN DELTA TEMP., DEG-F:                              117.64
  OVERALL TRANSFER COEFF. U, BTU/HR-SQ.FT-DEG F:            50
  TUBE ROWS:                                                10
  ESTIMATED FAN POWER, HP:                                  329.49
  EST. BARE TUBE SURFACE AREA, SQ.FT:                       42503.7
  ESTIMATED FACE AREA, SQ.FT:                               3362.63
  ESTIMATED WEIGHT, LBS.:                                   440505.09

**************************************************************************
```

**Typical printout** (above) of program used for gas cooling (Fig. 3). Below are Results of liquid cooling problem run by program (Fig. 4).

```
 TYPICAL HEAT TRANSFER COEFFICIENTS FOR AIR-COOLED HEAT EXCHANGER:

--------------------------------------------------------------------------
LIQUID COOLING                                              BARE TUBE U
 SERVICE                                                    (BTU/HR-SQ.FT-DEG F)
--------------------------------------------------------------------------
ENGINE JACKET WATER                                         120-130
FUEL OIL                                                    20-30
LEAN CARBONATE SOLUTION                                     90
LEAN AMINE, 15-20 WT.%                                      100
            20-25 WT.%                                      95
LIGHT GAS OIL                                               60-70
LIGHT HYDROCARBONS                                          75-95
LIGHT NAPHTHA                                               70
PROCESS WATER                                               105-120
RESIDUUM                                                    10-20
SULFINOL, 7 CP. OUTLET                                      70
TAR                                                         5-10
----------------------------------------------------------------------


THE RESULTS ARE :

**************************************************************************

AIR-COOLED EXCHANGER NO.:                                   E-510

--------------------------------------------------------------------------

  PROCESS TEMP., DEG-F:                     IN              200
                                            OUT             150
  AIR TEMP., DEG-F:                         IN              70
                                            OUT             130.65
  HEAT TRANSFER DUTY, MMBTU/HR:                             50

  LOG MEAN DELTA TEMP., DEG-F:                              70.67
  OVERALL TRANSFER COEFF. U, BTU/HR-SQ.FT-DEG F:            95
  TUBE ROWS:                                                4
  ESTIMATED FAN POWER, HP:                                  126.24
  EST. BARE TUBE SURFACE AREA, SQ.FT:                       7448
  ESTIMATED FACE AREA, SQ.FT:                               1477.78
  ESTIMATED WEIGHT, LBS.:                                   110833.34

**************************************************************************
```

```
TYPICAL HEAT TRANSFER COEFFICIENTS FOR AIR-COOLED HEAT EXCHANGER:

-------------- ---------------------------------------------------------
CONDENSING                                                BARE TUBE U
 SERVICE                                                  (BTU/HR-SQ.FT-DEG F)
------------------------------------------------------------------------
TOTAL CONDENSER:
AMINE REACTIVATOR                                         90-100
AMMONIA                                                   100-120
FREON 12                                                  60-80
HEAVY NAPHTHA                                             60-70
KEROSENE                                                  65
LIGHT GASOLINE                                            80
LIGHT HYDROCARBONS                                        80-95
LIGHT NAPHTHA                                             70-80
PENTANES THRU LIGHT NAPHTHA, 70 PSIG                      90
                             20 PSIG                      85
                             10 PSIG                      75
REACTOR EFFLUENT-PLATFORMERS,REXFORMERS,HYDROFORMERS      60-80
STEAM (0-20 PSIG)                                         130-140
STILL OVHD-LIGHT NAPHTHAS,STEAM & NON-CONDENSABLE GAS     60-70


PARTIAL CONDENSER:
HYDROGEN-RICH REACTOR EFFLUENT
  HYDROCRACKER,1400-3000 PSIG                             80
  CAT.REFORMER,350-450 PSIG                               75
  HYDROTPEATERS,NAPHTHA                                   70
  HYDROTREATERS,GAS OIL                                   60-70
CRUDE COLUMN OR STABILIZER OVHD                           65
CAT.CRACKER FRACTIONATOR OVHD                             75
------------------------------------------------------------------------


THE RESULTS ARE :

************************************************************************

AIR-COOLED EXCHANGER NO.:                                 E-201

------------------------------------------------------------------------

  PROCESS TEMP., DEG-F:                    IN             250
                                           OUT            150
  AIR TEMP., DEG-F:                        IN             75
                                           OUT            160.52
  HEAT TRANSFER DUTY, MMBTU/HR:                           100

  LOG MEAN DELTA TEMP., DEG-F:                            82.03
  OVERALL TRANSFER COEFF. U, BTU/HR-SQ.FT-DEG F:          80
  TUBE ROWS:                                              6
  ESTIMATED FAN POWER, HP:                                190.48
  EST. BARE TUBE SURFACE AREA, SQ.FT:                     15238.59
  ESTIMATED FACE AREA, SQ.FT:                             2005.00
  ESTIMATED WEIGHT, LBS.:                                 176446.78

************************************************************************
```

**Example printout** for condensing service use (Fig. 5).

tions presented in references 5 and 9.

Correlations for heat transfer coefficients are normally included in the dimensionless Nusselt number, which in turn is a function of the dimensionless Reynolds and Prandtl numbers. For tube bundles and finned tubes, the heat-transfer coefficients are also functions of the spacing, height, and thickness of the fins, and the spacing of the tube bundles.

After the individual heat-transfer coefficients (or heat-transfer resistances) are determined, the overall heat-transfer coefficient can be calculated based on the following:

$$U = \left(\frac{1}{h_o} + R_m + R_{if} + \frac{1}{h_i}\right)^{-1} \quad (1)$$

Nomenclature for all of the variables in the equations is shown in the accompanying box.

Factors affecting the individual heat-transfer coefficients, and consequently, the overall heat-transfer coefficient for air coolers can be found in the literature and in a number of textbooks. Therefore, they are not elaborated on here.

**Optimum bundle depth.** After the overall heat-transfer coefficients are keyed in to the computer, the program will determine the optimum bundle depth based on the effect of the temperature level and the overall heat-transfer rate upon the optimum bundle depth. Correlations of optimum bundle depth as function of $(T_1 - T_3)/U$ need to be established at this point for various tube sizes, tube material, tube and fin configurations, and spacing.

Optimum bundle-depth correlation, based on 1-in. OD × 24-ft long steel tubes with extruded aluminum fins, and 2⅜-in. triangular spacing published by E.C. Smith,[1] are adopted and employed in the program. For other tube sizes, tube material, tube and fin configurations, and spacing, new correlations need to be established and incorporated into the program.

If the optimum bundle depth determined is between 3 and 12, the program proceeds to read tabulated data on tube-row depth, bare-tube surface area per horsepower (P), unit weight per square foot of face area (G), typical face velocity (V), and square feet of surface area per square foot of face area (R). Again, tabulated data, published by E.C. Smith[1] for typical design face velocities for the various bundle depths, the ratio of bare tube surface area to square foot of face area, and the unit weight per square foot of face area for the various tube rows, are adopted in the program.

The surface ratio is based upon 1-in. OD tubing on 2⅜-in. triangular spacing. Actual selections during the process of designing the air coolers may be different from these tabulated data. Hence, similar data based on the actual selections have to be established.

In the case where the optimum bundle depth determined by the program is outside the range of 3 to 12, the computer will display a warning message. If the optimum bundle depth is less than 3, it is set to be 3 and then proceeds to the next calculation.

If the determined optimum bundle depth is more than 12, it is set to be 12 and then the program continues. In either case, the user may want to go back to analyze the current selection and redesign the air-cooled heat exchanger.

**Face area.** The next step is to determine the face area. First, an air temperature rise $(T_4 - T_3)$ is assumed. The program then calculates the total face area required, FA1, based on the assumed temperature rise, heat duty, and typical face velocity using the following equation:

$$FA1 = \frac{Q}{(T_4 - T_3) \times V \times 1.08} \quad (2)$$

It then calculates the log mean temperature difference (LMTD). If there is no temperature cross (outlet air temperature higher than outlet fluid temperature), the program continues to calculate the bare-tube surface area (A) using Equation 3:

In the case where there is an obvious temperature cross, the LMTD needs to be corrected based on the LMTD charts for cross flow.

$$A = \frac{Q}{U \times LMTD} \quad (3)$$

The program then divides the above calculated bare tube surface area required (A) by the ratio of surface area to face area (R) to obtain the required face area, FA2. If FA2 equals the FA1 calculated, within the convergence criteria, the program continues to the next step. Otherwise, a new temperature rise is assumed, and the calculation procedure is repeated until the convergence is reached. In this program, a convergence criterion of 0.005 is used.

After convergence is reached and the final face area determined, the horsepower required is obtained by dividing the total bare surface area required (A) by the ratio of bare-tube surface area per horsepower (P). The estimated air cooler weight is determined by multiplying the calculated face area (FA1) with the unit weight per square foot of face area (G). The program then proceeds to echo the input data and prints the calculated results.

**Examples.** Three examples (Figs. 3, 4, and 5) illustrate the typical overall heat-transfer coefficients and the outputs for gas cooling, liquid cooling, and condensing cooling. The input data, process fluid inlet and outlet temperatures, the ambient air temperature, and the total heat transfer

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duty, are echoed in the printout with the calculated results.

The overall heat-transfer coefficients selected (or calculated if desired) and the program calculated air outlet temperature, the log mean temperature difference, the tube rows, the estimated fan power, bare-tube surface area, face area, and the estimated weight of the air coolers are all included in the printout.

Note that the typical overall heat-transfer coefficients, U, are displayed for the user's convenience only. The user always has the option to simply select the coefficients from the tables displayed, or enter a coefficient from another source. Again, the user may want to calculate the overall heat-transfer coefficients by rigorous methods.

**Limitations.** It should be understood that the program is intended for the estimate and preliminary sizing of air-cooled heat exchangers only, and not to be used as a tool for the final design. There are a number of leading designer-manufacturers of air coolers who not only manufacture finned tubes but also rate air coolers and specify the fans, the air-flow requirements, and the spatial requirements.

However, the program will prove valuable to users and purchasers of air-cooled exchangers because they will be able to provide better preliminary information to the manufacturer during the request for quotations.

Specific correlations and data included in the program are based on certain tube sizes, tube material, tube and fin configuration, and spacing. For a specific application, other correlations and data may need to be developed and incorporated into the program before it can be correctly used.

Correlations for rigorous heat-transfer coefficients and pressure drops can be added to increase the capability and flexibility of the program. Information on pricing of the air coolers can be incorporated into the program for optimization purposes.

Although there are certain constraints and limitations on using the program due to the complexity of an air-cooler design, the program presents an expedient way for air cooler estimates and preliminary sizing. It alleviates the painful experience of having to do these trial-and-error calculations by hand.

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**COMPRESSOR CONTROL—1**

# Parallel centrifugal gas

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Energy efficiency of parallel, centrifugal gas compressors can be improved by controlling the compressors to unload simultaneously to their surge limts.

Simultaneous unloading to the surge limits can also allow more precise pressure control, provide better compressor protection, and allow simpler automated control systems.

Specific power consumption is also offered as an improved definition of energy efficiency. Because polytropic efficiency, the most common efficiency measure, defines only the energy efficiency to compress a gas between the inlet port and the discharge port of a compressor, it does not account for the efficiency of gas delivery to the user. Specific power consumption includes energy costs that must be paid for but which are not accounted for by polytropic efficiency.

This first of two articles discusses the concept of simultaneous loading and unloading of centrifugal compressors and compares the method with other control strategies. The concept of specific power consumption is also defined.

The conclusion will describe an algorithm for simultaneous loading and unloading to the surge limit.

The efficiency and reliability of centrifugal compressors can be severely limited by the control system. Less-than-effective controls, rather than mechanical design, is often the cause of lost efficiency, shutdowns, and damage.

In many installations, load changes are anticipated for parallel compressor operation. The Load changes on a 24 hr, weekly, or seasonal cycle. However, in many installations examined by the authors, less-than-adequate provisions have been made in the control system for these load changes.

Often, load control is manual and very costly in terms of wasted energy and lessened reliability. Whether the load control is manual or automatic, it can, in the authors' opinions, be improved significantly.

In some installations, load changes are not anticipated, steady load being predicted. But only in a perfect world would load demand never change. Only in a perfect world would a station always operate in steady state at the design point of each compressor.

In the real world, many operations that have been designed for steady state at full load have been forced, as experience shows, into load changes. Economic cycles or other events beyond our control may have reduced user demand.

Changes in the feedstock or improvements in process design may have changed the compressor load. Moreover, mechanical or control failures in any part of the process may any time forcibly change the load.

A more realistic approach is to design the control system of a compressor station to cope safely and efficiently with substantial load changes. This approach leads also to more-precise and more-stable pressure control, better machine protection and improved automation.

**Current control strategies.** Many different strategies have been employed to unload and load a compressor station. One common method is to set the speed control manually and run each compressor continuously at full load.

Swings in station load are met by recirculation of gas around the compressors. This system obviously wastes energy.

Biasing flow is another common station control method. This method employs a primary or station pressure controller plus separate flow controllers on each compressor.

Flow controllers are adjusted to divide the flow between the station compressors in some ratios according to their performance characteristics, e.g., 50%, 35%, and 15%. This system requires constant readjustment as operating conditions change and has other shortcomings. A similar problem will be found with station control strategies that bias compressor speeds.

Another very common method calls

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Based in part on a paper presented at the ASME International Gas Turbine Conference, Dusseldorf, West Germany, June 8-12, 1986.

# compressors can be controlled more effectively

for base loading the most efficient compressors either at their maximum flow or at their point of maximum polytropic efficiency. The swings in demand load are then met by modulated control of the less-efficient compressors, or by on-off control of these compressors. This system is not energy efficient or sufficiently reliable in our opinion.

We believe that all the above methods can be improved. In our analysis, we shall attempt to show:

- Simultaneous loading and unloading of the compressors is the most effective station strategy. Properly controlled, it gives the most energy efficiency, the most precise control, better machine portions, and improved automation.
- Reducing recycle is the most important component of station energy efficiency. Put another way, station control strategy requires an effective antisurge system for energy efficiency, as well as for machine protection.
- Regardless of variations in compressor polytropic efficiency, the station should unload so that all the compressors reach their surge control lines simultaneously.

**Improved efficiency definition.** First, let us carefully review the definition of compression energy efficiency. We believe the measurement commonly used, polytropic efficiency of

Fig. 1

Centrifugal gas compressor

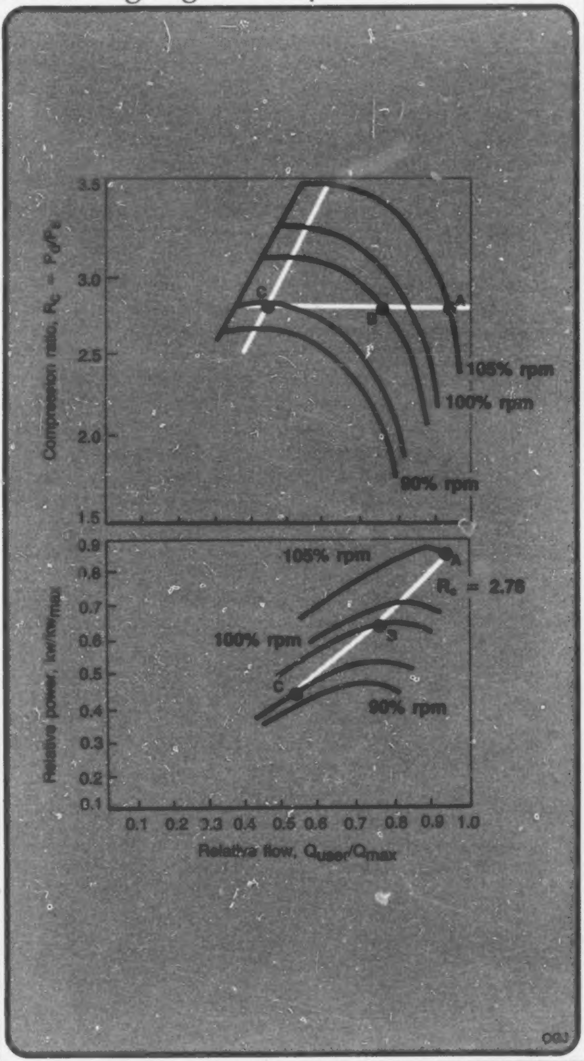


Fig. 2

Single compressor specific power

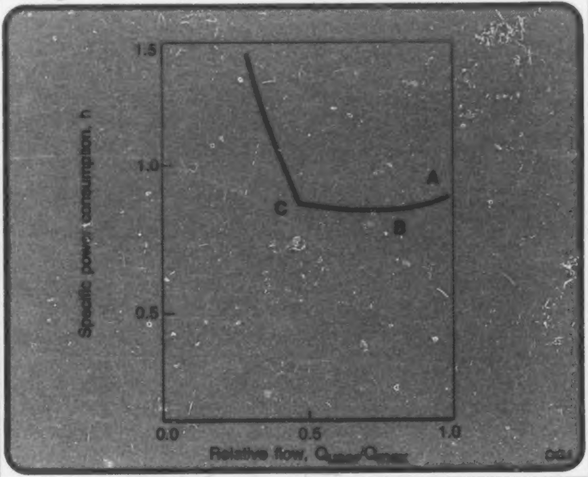
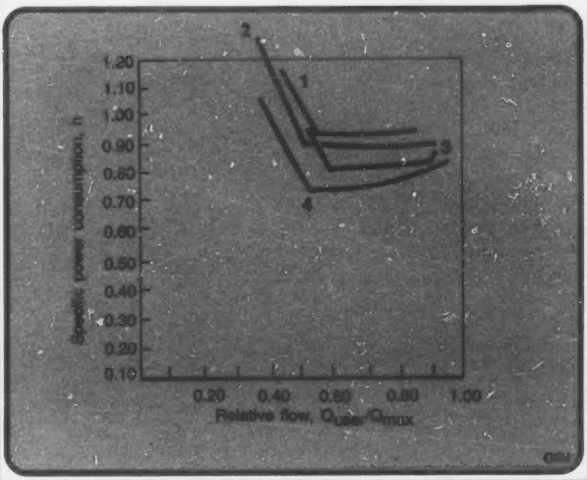


Fig. 3

Specific power of four compressors



the compressor, has major limitations.

Polytropic efficiency defines the energy efficiency required to compress the gas between the inlet port and the discharge port of the compressor. However, this is not the energy efficiency of gas delivered to the user, a point of great importance.

In normal compressor operation, there can be substantial energy losses between the discharge port of the compressor and the discharge header, where the gas is delivered to the user, process, or pipeline. In a compressor system, major energy losses can occur through the antisurge valve or through cooling or quenching, all as a part of normal operation.

Instead, we shall propose a wider definition of energy efficiency, which we term the specific power consumption, h. It can be defined as follows:

Specific power consumption, h, is the energy input to a comressor system required to maintain the controlled gas parameter, and divided by the number of flow units of gas delivered to the discharge header. It may be defined in absolute units, $h_a$, or in relative units, $h_r$.

For example, if it takes 500 kw of power to deliver 1,000 standard cubic meters/minute (scm/min) of gas at a compression ratio of 2, then in absolute values,

$$h_a = 0.5\frac{\text{kw}}{\text{scm/min}}$$

Units are power divided by flow rate.

In order to compare efficiencies of compressors of different capacities and power consumptions, it is convenient to use a dimensionless measurement for specific power consumption. Units are power divided by maximum power, and flow rate divided by maximum flow for a specific compressor.

$$h_r = \frac{\text{kw}}{\text{kw}_{\text{max}}} \times \frac{\text{scm/min}}{\text{scm/min}_{\text{max}}} \qquad (1)$$

Because h increases with energy consumption, note than an increase in h is a decrease in system energy efficiency, and vice versa.

Specific power consumption, therefore, includes energy costs that must be paid for, but are not measured by polytropic efficiency. The authors belive that specific power consumption gives a more realistic measure of the economic costs of a compression system.

## Control strategies compared

Compressors may be loaded and unloaded by speed changes, changes in guide vane position, throttling, or recirculation. We shall use for our examples centrifugal gas compressors with variable speed gas-turbine drives and recirculation, controlled for compression ratio.

Analogous results would follow if the controlled parameter was inlet pressure, discharge pressure, or flow rate.

The reasoning and results would be analagous, too, if the compressors were controlled by adjustable inlet guide vanes or throttles.

The strategy selected for sequencing compressors, loading and unloading, and the algorithm controlling loading and unloading, significantly influences the station efficiency, as we shall show. Three strategies will be analyzed for specific power consumption under different loading and unloading strategies. We shall compare these loading and unloading strategies for their energy efficiency, machine protection, and automation.

**Minimum safe flow.** A centrifugal compressor may be unloaded only to its surge limit line. At that limt, dangerous flow and pressure oscillations begin which can damage or destroy the compressor.

To protect the compressor from surge damage, gas is recycled through the antisurge valve (also known as the recycle or bypass valve), before the surge limit is reached. The control line where recycle begins is the surge control line.

We may consider this to be the line of minimum safe flow. The calculation of the minimum safe flow is complex.

There is a different minimum safe flow for each compressor inlet pressure, head, speed, inlet temperature, gas composition, and position of guide vanes.

The minimum safe flow will also vary substantially, depending on the effectiveness of the surge control system. The more effective the surge control, the closer the surge control line will be to the surge limit line, and the less the recycle needed.

**Specific power consumption.** The unloading of compressors within the station may be simultaneous, successive, or mixed. The most efficient strategy can be found by comparatively simple calculations based on an analysis of the performance map of each compressor in the station.

Suppose a station of two identical compressors operating in parallel. Fig. 1 gives the performance curves for two identical gas compressors built by a leading European manufacturer.

Assume that a user or process requires that the station maintain a constant compression ratio, $R_c = 2.75$. Note that the reasoning which follows would apply equally well if the controlled parameter were discharge pressure, suction pressure, or flow.

**Single-compressor operation.** The specific power consumption, $h_r$, plotted as a function of the gas flow rate is shown for single compressor operation in Fig. 2. Points A, B, and C lie on a line of constant compression ratio but varying flow rates.

Point A belongs to the maximum performance curve corresponding to the maximum speed and flow. At Point B, the design point (the expected operating point of the compressor), the speed and flow rate are somewhat lower.

The specific power consumption at B has decreased slightly, which indicates an increase of efficiency. Point C lies on the compressors's surge control line.

Between Points B and C, the specific power consumption has increased slightly and the efficiency decreased slightly. At Point C, however, efficiency is still higher than at the initial Point A.

Point C is the minimum safe flow for this compressor at this speed, with these inlet conditions, and with some specific surge control system. From Point C, a further decrease of the station flow cannot be safely effected by a further decrease of flow through the compressor.

To prevent surge damage, the difference between the station demand flow and the minimum safe flow through the compressor must be recirculated to the suction network. Under such circumstances, the flow to the user decreases.

But, the flow through the compressor is constant at C and the compressor power is constant. As a result of this recirculation, the specific power consumption sharply increases to the left of Point C. Put in alternate terms: The system efficiency of any compressor drops sharply once recirculation begins and the cost of compressing a flow unit of gas rises sharply.

The effectivenss of the surge control system now becomes critical. The more effective the surge control system is, the narrower the recirculation zone can be. A less effective surge control system will require that the safety margin between the surge control and surge limit lines be increased.

An increase of safety margin by only 5% will decrease the efficiency at Point C by about 10%. Effective surge control systems have been previously described by the authors.[1]

In contrast, the change in polytropic efficiency before recirculation begins is not significant at all. The authors have analyzed more than 200 centrifugal and axial compressors controlled by speed, adjustable guide vanes, or throttles.

Fig. 4

Unloading of identical compressors

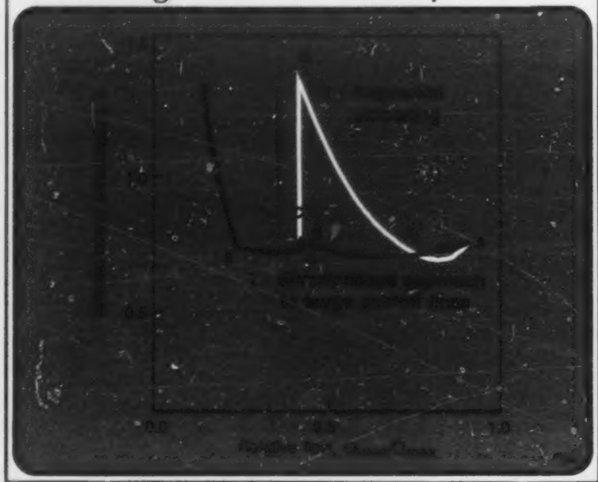
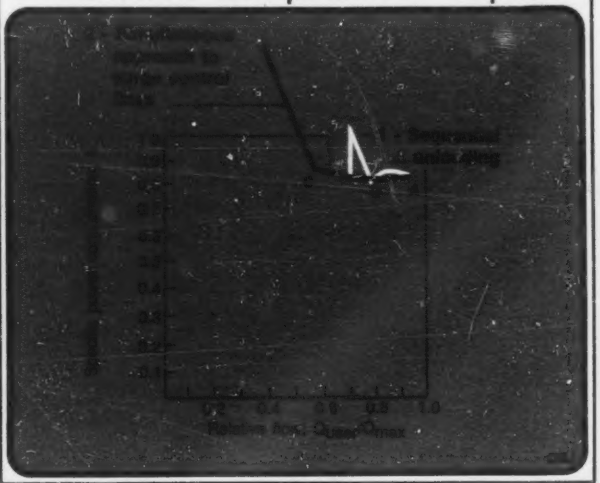


Fig. 5

Two different compressors compared



This analysis indicates that the specific power consumption either stays steady as the compressor flow decreases to the surge control line or, in some cases, increases slightly and then decreases slightly. However, the specific power consumption increases dramatically as soon as recirculation begins.

As further examples, Fig. 3 shows the specific power consumption as a function of flow rate for compressors of four other leading American and European compressor manufacturers. This illustrates our first conclusion for improving the efficiency of compressor operation.

- Increasing the safe operating range without recirculation is more important for compression efficiency than maintaining the compressors operating point at the point of highest polytropic efficiency.

**Multicompressor operation.** We will now examine the parallel operation of two or more compressors. Suppose the sample station has two identical compressors.

A constant compression ratio must be maintained for this sample station, and the station flow must be adjusted to meet the demand. Note, again, that suction pressure control or discharge pressure control give analagous results.

There are three major alternatives to changing station flow:

- Unload and load compressors simultaneously.
- Unload and load compressors in sequence, first decreasing the flow of the least efficient compressor and keeping the others at maximum load.
- Combine the simultaneous and sequential unloading strategies.

**Simultaneous unloading/loading.** Fig. 4 shows the specific power consumption of a simultaneous approach to the surge control lines vs. sequential loading/unloading for these two identical compressors in parallel operation. The performance characteristics of these compressors have already been discussed (Fig. 1).

The compression ratio of the station will be maintained during unloading. Again, note that analogous results obtained if the controlled parameter was suction pressure, discharge pressure, or flow.

Curve 1 of Fig. 4 (A,B,C,D,E) shows in relative units the change of specific power consumption using simultaneous unloading of the station. Exactly as with the single compressor, the station efficiency first increases slightly and then decreases slightly between the maximum station capacity (Point A) and the minimum safe flow (Point B).

Both compressors approach their surge control lines at B simultaneously. Between Points B and C, the station output is adjusted to the lower gas demand by partial recirculation around the compressors.

At Point C, compressor No. 1 is shut down. The control system compensates for this flow loss by loading compressor No. 2 to its maximum speed (Point D). Then, the station is further unloaded by reducing the speed of compressor No. 2 down to its surge control line (Point E). Further decrease in flow to the user is compensated once more by recirculation.

Between Points B and C, the efficiency of the station drops but, after the shutdown of compressor No. 1, it increases at D to the efficiency observed at the initial Point A. Efficiency changes insignificantly from D to Point E, after which it drastically decreases. Between Points A and E, there is no significant change of the station efficiency.

**Sequential unloading/loading.** The dotted curve 2 of Fig. 4 corresponds to sequential unloading/loading. Between Points A and F, compressor No. 1 base loaded and remained at its maximum speed. Compressor No. 2 is unloaded down to its surge control line (Point F). The efficiency with sequential unloading is less in this segment of Curve 2 than the efficiency under simultaneous unloading.

At Point F, it is not possible to shut down compressor No. 2 because it would be impossible to deliver the flow demand. Should compressor No. 2 be shut down at this time, the flow, the compression ratio, and the pressure at the discharge of the station will drop below their required levels.

To shut down one compressor without disturbing the required pressure is possible only at Point G, where the station efficiency is extremely low. Shutting compressor No. 2 down at G, the station efficiency is extremely low. Shutting compressor No. 2 down at G increases the station efficiency to Point D.

From Point D to Point E and beyond there is no difference between Curves 1 and 2 in efficiency.

Curve 2 is nearly always higher in specific energy consumption than Curve 1 between Points A and D. This proves, in our opinion, that simultaneous unloading is far more efficient, but only if all compressors reach their surge control lines simultaneously.

For the overwhelming majority of compressor stations equipped with two or more centrifugal compressors, unloading by a simulatneous approach to the surge control lines if the first condition for higher station energy efficiency at at gas demand levels.

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Naum Staroselsky is president of Compressor Controls Corp. This year, he received the Innovator of the Year award from the U.S. Small Business Administration. Staroselsky holds a PhD in mechanical engineering from the Leningrad Polytechnical Institute, and he holds 21 patents related to turbomachinery. He has published over 20 technical articles on turbomachinery and control and has lectured extensively throughout the world.

Lawrence Ladin is president of Ladin Energy Services Inc., a supplier of industrial and commercial lighting systems. He was chairman and co-founder of Compressor Controls Corp. and was involved in its marketing and finance.

Ladin holds a BS degree in Mathematics from the University of Minnesota and is a member of the Instrument Society of America.

Some reflection will show that this conclusion applies to compressors operating in series, as well as in parallel.

**Precise pressure control.** Besides improving energy efficiency, the simultaneous approach to the surge control lines has dynamic control advantages too. It can give faster and more precise control of station pressure. When the flow demand by the user changes, the pressure differential across the station also changes. This changes, in turn, the flow through each compressor.

If the control system changes the performance of only one compressor at a time then the overall response time of the system increases. In control terminology, the gain decreases.

In order to compensate for the loss of the system gain and to make system response time faster, it is necessary to increase the speed of response of each controller. However, this is difficult to do in some cases because system components such as the valves and transmitters become the limiting factors.

**Machine protection.** Comparing the two strategies with regards to machine protection, the simultaneous approach to the surge control line again has the advantage. With simultaneous unloading, the compressors spend a minimum time on their surge control lines as compared to sequential unloading. This is an important feature for damage control, because operation on the surge control line always carries some risk of surge and surge damage.

The compressors also spend less time at their load limit or speed limit, another advantage for machine protection. There are fewer starts and stops, which is a third advantage.

**Automation.** Automation is easier with the station having simultaneous loading and unloading. Shutting down a compressor is not indicated until the station flow has dropped to 30%.

With sequential unloading, shutting down a compressor is indicated at 50% of station flow. Therefore, there is less need for operator intervention with simultaneous unloading.

The same reasoning applies to loading the stain. There will be fewer start ups with simultaneous loading.

**Compressors of different sizes.** Selecting the unloading/loading sequence for parallel-operated centrifugal compressors may become more complicated when the size, power, and efficiency of the compressors are different. Suppose, for example, that one of the two parallel working compressors is slightly more efficient (Curve 2, Fig. 3) than the other compressor (Curve 1, Fig. 3). The more efficient compressor also has the higher maximum flow and a wider range of operation without recirculation.

Fig. 5 compares the simultaneous approach to the surge control line (Curve 2) and sequential unloading (dotted Curve 1). In the sequential unloading, the less efficient machine is first unloaded to its surge control line. Between Points A (maximum station capacity) and B (the surge control line of the less efficient machine) the station efficiency under the sequential or simultaneous unloading does not show any significant difference for these compressors of slightly different efficiency.

At Point B, efficiency drops drastically under sequential unloading. In contrast under the simultaneous approach to the surge limits, the efficiency remains high until Point C. At C, both compressors must begin recirculating. Supposing a high difference in capacity or efficiency of not more than 7%, a simultaneous approach to the surge control lines is the most efficient strategy.

With compressors of significantly different efficiencies (more than 10%) mixed unloading or sequential unloading may be more efficient, in our opinion. However, such stations are few in number.

**Reference**

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# Compressors simultaneously approach surge

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A control algorithm has been developed to allow control of parallel gas compressors so that they unload simultaneously to their surge control limits. Equations describing the algorithm, the S Criteria, are given along with a description of how the control system operates.

A description and the operating characteristics of the concept, used on an offshore gas compression station, are discussed. The first installment of this two-part article, OGJ, Nov. 3, p. 78, discussed the advantages of simulation control to the surge limit, and compared the concept with other common control methods.

**S. Criteria.** There are many possible algorithms for simultaneous approach to the surge control lines of centrifugal compressors. Obviously, each algorithm depends on measuring the distance from the operating point to the surge control line.

Because compressors may differ in capacity and characteristics, the absolute distance of the operating point from the surge control line is not useful.

We recommend using a dimensionless number expressing the relative distance from the surge control line. This measurement technique will now be incorporated into a control algorithm.

The algorithm that will be described here is called the "S Criteria." It is one possible method of improved control. The S Criteria was developed and patented by one of the authors.

This approach to loading/unloading is of value for:

- Controlling a simultaneous approach to the surge limit by all the station compressors
- Increasing station energy efficiency
- Improving precision and speed of pressure control
- Improving machine protection
- Improving automation.

**Surge line equation.** To calculate S, the relative distance from the surge control line of any compressor at any given moment, we must begin with the equation of its surge control line. Many equations have been offered for the surge control line. In a previous publication by the authors,[1] one useful equation was defined as

$$K\,\Delta P_c + b = \Delta P_{o,s} \qquad (2)$$

where:

K is a constant defining the slope of the surge limit line

$\Delta P_c$ is the pressure differential across the compressor

$\Delta P_{o,s}$ is the pressure differential across a flow measuring device in the compressor suction

b is a constant defining the distance in some flow unit between the surge limit and the surge control line.

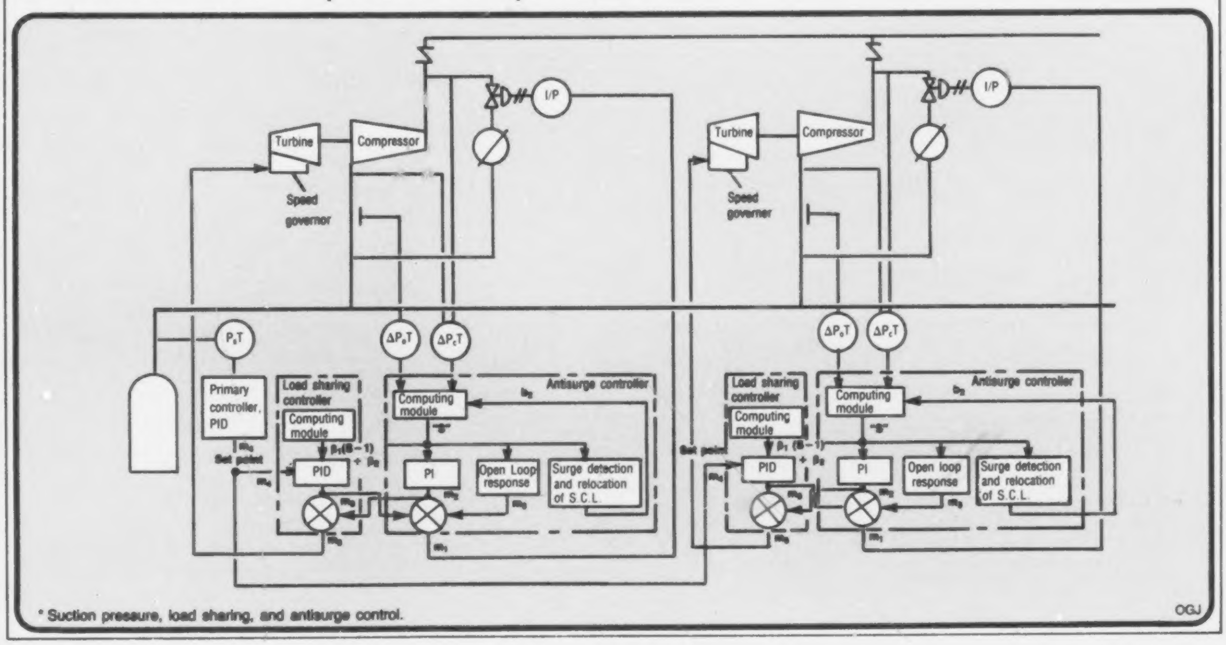
This equation is valid for compressors with constant geometry, stable gas composition, and a surge limit that is linear in the coordinates $\Delta P_c$ and $\Delta P_{o,s}$. The equation is self compensating for inlet temperature changes.

Another equation widely used to calculate the surge control line is:

$$f\,\frac{\Delta P_c}{P_s} + b = \frac{\Delta P_o}{P_s} \qquad (3)$$

Fig. 6

S Criteria controls parallel compressors*



* Suction pressure, load sharing, and antisurge control.

OGJ

Fig. 7

Concept controls load sharing

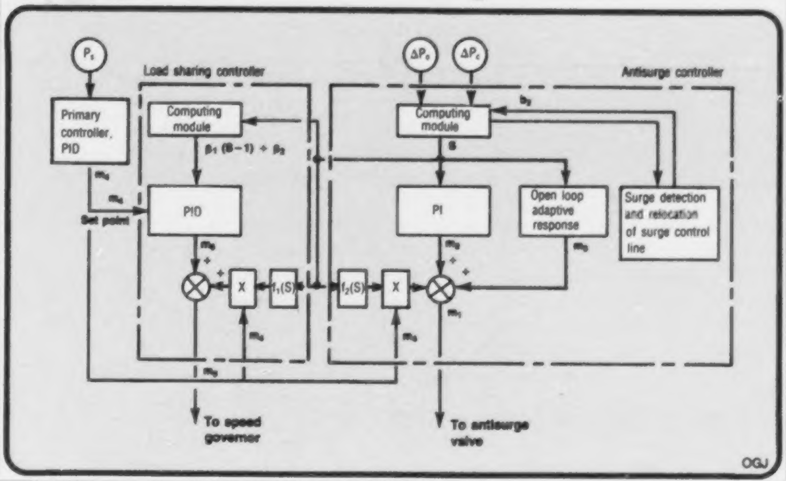
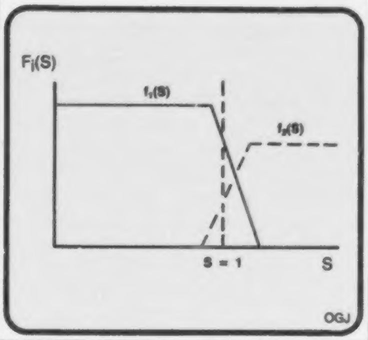


Fig. 8

f₁ and f₂ of S Criteria



where:

$P_s$ is the compressor suction pressure (also see nomenclature box).

Equations of more complexity are recommended for compressors with variable guide vanes, for gases with variable composition, or for compressors with irregular surge limit lines. However, the simple but widely useful Equations 2 and 3 will suffice for this example.

**S Criteria equation.** Based on Equations 2 and 3, we define S as follows:

$$S = \frac{K\,\Delta P_c + b}{\Delta P_o} \quad \text{or}$$

$$S = \frac{f\,\dfrac{\Delta P_c}{P_s} + b}{\Delta P_o / P_s} \qquad (4)$$

If S is less than 1, the operating point is in the safe zone. The lower the value of S, the greater the safe distance from the surge control line.

When S is equal to 1, it corresponds to a compressor operating point located just on the surge control line. An S more than 1 corresponds to the operating point having crossed the surge control line and moved toward surge.

There are two alternatives to calculate the deviation "e" of a compressor's operating point from the surge control line.

The first is:

$$e_1 = S - 1 \qquad (5)$$

The second is:

$$e_2 = f\,\frac{\Delta P_c}{P_s} + b_1 - \frac{\Delta P_o}{P_s} \qquad (6)$$

$$e_2 = \frac{\Delta P_o}{P_s}$$

$$\frac{f\,\dfrac{\Delta P_c}{P_s} + b_1}{\Delta P_o / P_s} - 1 \qquad (7)$$

or

$$e_2 = \frac{\Delta P_o}{P_s} (S - 1) \qquad (8)$$

or

$$e_2 = \frac{\Delta P_o}{P_s}\, e_1 \qquad (9)$$

Using $e_1$ in the control algorithm, it is possible to ensure stable operation over the whole range of operating conditions even with a high controller gain. This provides faster, better quality, more precision control.

**S Criteria control.** Fig. 6 shows a station controlled by S Criteria for suction pressure, having two centrifugal gas compressors with gas-turbine drives. The primary, or station, controller maintains suction pressure. Each compressor has a load-sharing controller that divides the station load, plus an antisurge controller.

The antisurge controllers of compressors No. 1 and No. 2 calculate the criteria S for their respective machines. Each antisurge controller sends its calculated S value to the calculating module of its companion load-sharing controller.

The calculating module of each load-sharing controller computes the value

$$S' = \beta_1 (S - 1) + \beta_2 \qquad (10)$$

This is a universal equation that can be used for any compressor sequencing. By tuning $\beta_1$, it is possible to individually control the rate of change of flow from each compressor between its maximum load and surge control line. This can further improve station efficiency.

If $\beta_2$'s for both compressors are equal, then regardless of the values of $\beta_1$, under decreasing flow, both compressors No. 1 and No. 2 will reach their surge control lines ($S = 1$) simultaneously. If $\beta_2$'s are unequal, the compressors will reach their surge control lines sequentially. This permits any sequencing desired.

The $\beta_2$ value goes to the proportional-integral-derivative (PID) part of the load-sharing controller as its control variable. One single set point for all load-sharing controllers is developed by the primary station controller, which maintains constant station inlet pressure.

The control shown in Fig. 6 is a typical cascade control. The primary controller develops the set points for all the secondary controllers.

As is well known from control theory, the stability of cascade control can be achieved only if the secondary controllers are much faster than the primary controller. However, with this controller tuning, when the flow demand changes, the load-sharing controllers would first change the speed of a compressor in a direction opposite to that required to adjust station output to the gas demand. This would increase deviation of suction pressure from its required level and would make the time of the transient process longer. There are two alternatives to avoid the decrease of dynamic precision while using this cascade control scheme.

The first alternative is to install a dynamic filter between the antisurge controller computing S' and the load-sharing controller using S' as its process variable. Such a filter presents a rough model of the controlled object, and it permits the primary controller to rapidly change the set point of the load-sharing controllers and correctly change the speed of the compressors

Fig. 9

Station controlled by biasing flow

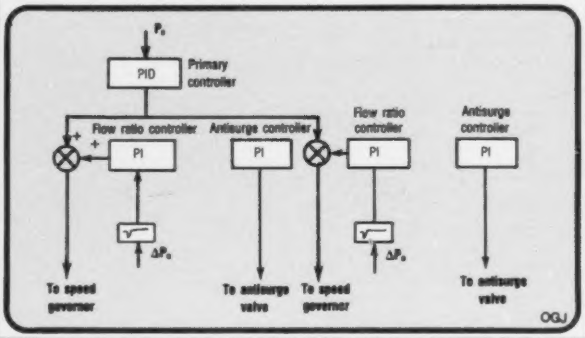
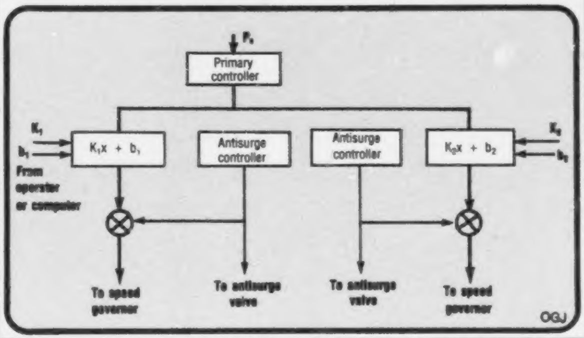


Fig. 10

Control by biasing compressor speed



to immediately restore pressure to the required level.

The second alternative, patented by one of the authors, is to send feedforward adaptive signals from the primary controller directly to the control members, temporarily bypassing cascade control. The principal schematic of the authors' solution is given in Fig. 7.

The output of the primary station controller not only enters the load sharing controller as its set point, but it also enters the multiplication modules of both the antisurge controller and load-sharing controller. The outputs of these controllers can be defined as:

$$m_1 = m_2 + m_3 + f_2(S) \times m_4 \qquad (11)$$

$$m_5 = m_6 + f_1(S) \times m_4 \qquad (12)$$

The functions $f_1(S)$ and $f_2(S)$ are shown in Fig. 8

Making $f_1(S)$ variable permits reducing the gain of the primary or station controller via the load-sharing controller as the operating point of compressor approaches the surge control line. To complete the control system, the primary controller has a symmetrical connection where the gain to the output of the antisurge controller is increased as the operating point approaches the surge control line.

Thus, the primary or station controller switches from controlling the speed to controlling the position of the recycle valve while approaching surge. The controllers in this scheme should be set so that the primary controller will be much faster than the load-sharing controllers. Then, during changes in gas flow, the station pressure will be controlled first, and the load sharing controller will divide the total compressor station flow between the compressors the optimum way.

This scheme achieves energy economy with excellent steady-state precision and dynamic precision. Since the compressors spend a minimum of time on their surge control lines or speed limit lines, it adds to machine protection, especially since the number of starts and stops are minimized too.

The use of advanced antisurge controllers adds significantly to the machine protection. Control is self-compensating and needs no adjustment over a very wide range of changes in inlet pressure, inlet temperature, or flow demand. It, therefore, lends itself to improved automation.

**Other control strategies.** Suppose the controlled parameter is discharge pressure and the station consists of two centrifugal gas compressors with gas-turbine drives with speed control. Fig. 9 shows the station controlled by biasing flow. Fig. 10 shows the station controlled by biasing speed. (Biasing the position of the guide vanes or inlet throttle would be analagous control schemes.)

In both cases, the settings for each load controller, whether they are controlling by speed or flow, are valid for only one set of inlet conditions.

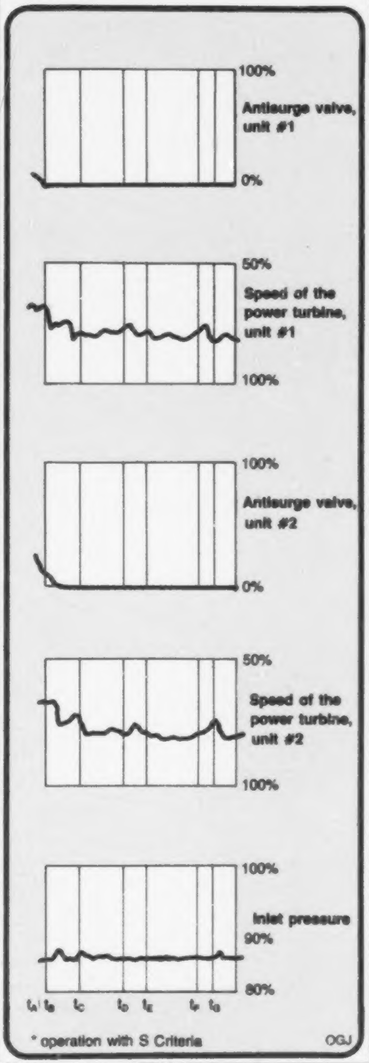
A glance at the compressor performance map confirms this. The intersection of the discharge pressure control line and the surge control line for each compressor will correspond to a different speed, or flow rate, or guide vane position whenever inlet conditions change. That is to say, any change in suction pressure, suction flow, temperature, or molecular weight.

Therefore, a simultaneous approach to the surge control line will require retuning of the controllers for optimum load distribution. This is a nearly impossible task for an operator and no easy task for a computer.

A second defect of these commonly used systems is the interaction of the independent surge control loops with the pressure control. The surge controller attempts to decrease discharge pressure and increase inlet pressure, while the pressure control system attempts to maintain discharge pressure.

Fig. 11

Compressor station*



* operation with S Criteria

These are incompatible goals and the quality of one or more of the control loops is seriously affected. Oscillation or "hunting" is likely to occur from time to time. Manual control

# Nomenclature

| | |
|---|---|
| $b$ | Distance between surge limit line and surge control line, dimensionless |
| $e$ | Deviation of operating point from surge control line, dimensionless |
| $h$ | Specific power consumption |
| $h_a$ | Specific power consumption, absolute units |
| $h_r$ | Specific power consumption, relative units |
| I/P | Current-to-pneumatic transducer |
| $K$ | Slope of surge control line, dimensionless |
| kw | Power, kw |
| $kw_{max}$ | Maximum power, kw |
| $m_1$ | Output of antisurge controller |
| $m_2$ | Proportional plus integral output of antisurge controller |
| $m_3$ | Open loop output of antisurge controller |
| $m_4$ | Output of performance controller |
| $m_5$ | Output of load-sharing controller |
| $m_6$ | Proportional plus integral plus derivative output of load-sharing controller |
| PI | Proportional plus integral control algorithm |
| PID | Proportional plus integral plus derivative control algorithm |
| $P_s$ | Pressure in compressor suction, bar |
| $Q_{user}$ | Flow to user, standard cubic meters/minute |
| $Q_{max}$ | Maximum flow, standard cubic meters/minute |
| $R_c$ | Compression ratio, dimensionless |
| rpm | Revolutions per minute |
| $S$ | Relative distance from surge control line, dimensionless |
| scm/min | Flow rate, standard cubic meters/minute |
| $scm/min_{max}$ | Maximum flow, standard cubic meters/minute |
| T | transmitter |
| $\beta_i$ | Normalizing coefficients for scaling Criteria S, dimensionless |
| $\Delta P_c$ | Pressure differential across compressor, bar |
| $\Delta P_{o.s}$ | Pressure differential across flow measuring device in compressor suction, mm $H_2O$ |

intervention would be needed to stabilize the system.

**A field installation.** An example of these theories in operation is taken from an offshore gas compression station equipped with two gas-turbine-driven compressors. The gas supply to this station has both large and fast changes in flow rate.

The simultaneously loaded and unloaded compressors use the S Criteria for load sharing to maintain stable suction pressure. The controllers are of the advanced type designed by one of the authors. The controls described are in continuous operation today.

The station control system is shown in Fig. 6. Fig. 11 shows a strip-chart record of inlet pressure, speed changes of the turbines, and response of the antisurge valves.

The gas supply to the station at the time $t_A$ is low. At $t_A$, both compressors are operating at low speed (70% of the maximum speed of the power turbine for unit No. 1 and 68% of the maximum speed for unit No. 2).

Both antisurge (recycle) valves are partially open, and the gas supply is starting to increase. The control system simultaneously closes both antisurge (recycle) valves in response.

A sharp increase in gas supply momentarily causes inlet pressure to increase at time $t_B$. The control system rapidly increases the speed of both compressors to restore inlet pressure to the required level.

After a slight decrease, the gas supply increases again sharply at time $t_C$. Again, the control system maintains the inlet pressure by rapidly speeding up both compressors. The control system maintains stable inlet pressure under further sharp fluctuations of the gas supply during the time intervals $t_D$ to $t_E$ and $t_F$ to $t_G$.

In general, the deviation of the inlet pressure from its required level never exceeded 2%.

The record (Fig. 11) shows the precise control, fast response, and control stability possible with simultaneous approach to the surge control lines using the S Criteria.

Note that the recycle is very low due to:

- The simultaneous approach to the surge control lines using the S Criteria
- The advanced antisurge control.

A comparison of before and after energy efficiency is not possible in this case because the control system is an original installation, not a retrofit. Machinery repairs have been minimal, and the need for operator intervention or manual control is negligible.

User reports to the authors indicate that if considerable load variation exists, an energy savings between 10% and 30% can be anticipated. Even when the load is stable, significant benefits can be expected from precise pressure control, improved machine protection, and improved automation.

Though much attention has been paid to more efficient compressor design, the control systems, which strongly influence operating efficiency and reliability, are often neglected.

Experience shows that we cannot commit the future; that is, we cannot guarantee stable operating conditions, good machine maintenance, or trained operators. The authors believe, therefore, that the control system should be designed to ensure safe, efficient, automatic operation under all possible operating conditions. ▪

# Pneumatic crude-unit controls modernized

**C. W. Alworth**
**D. A. Evens**
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Advanced control of a pneumatically controlled plant with a modern distributed digital instrumentation system is possible without replacing existing pneumatic transmitters and control elements. The control system sensors may have to be augmented, but they do not have to be replaced.

A modernized control system for a pneumatically controlled crude topping unit (CTU) at Conoco Inc.'s Ponca City, Okla., refinery was recently started up.

Pneumatic instruments are not proposed for new, grassroots plants, in spite of the comfort and experience with that instrument type. Electronic instruments are as reliable, they have no hysteresis, and they are easier to maintain than their pneumatic counterparts.

**The project.** Conoco operates a 65,000+ b/sd crude topping unit as its No. 1 CTU at Ponca City.

The unit was built in the early 1950s using the best instrumentation available. (Remember the old case instruments and mercury-filled DP cells?).

In the late 1960s and early 1970s a new control room was built for this unit, and the "newer-style" pneumatic instruments were installed. New field transmitters were purchased, new tubing runs were made, new thermocouples (TCs) and wires were installed, etc. The plant was put into A-1 shape, but it was still pneumatic.

A few years ago the unit engineer contacted our group (we provide instrumentation services to the entire corporation) to ask what could be done to upgrade the instrument system. Of particular interest was: better control of product final boiling points (end points), a better way to control tower side heat removal (pumparound), and some way to stabilize the tower on crude changes.

Our group gave the request considerable thought and proposed a demonstration project. The project was to look at several control techniques, one at a time, and attempt to prove the viability of each of these techniques to the refining management.

The project was to be based around the eight process instrument diagram (PID) loop Texas Instruments PM 550 programmable logic controller (PLC).

**Demo system.** The demonstration system consisted of:

- An eight-loop PM 550 with 7K memory
- A loop access module
- An annunciator panel (eight points)
- Two, six-pen recorders with patch panel
- An uninterruptable power supply
- Eight discrete output points (logic)
- Twenty thermocouple (TC) inputs
- Thirty-six pneumatic inputs
- Eight pneumatic outputs via an input/output (I/P) rack
- Four, 4-20 ma outputs (usually patched to recorders).

The system was placed in the CTU control room in May 1982. (It is still in use on another unit in the same control room).

We tubed up and sat back to decide what scheme we would try first.

To the operators, this system was a computer. It was our job to prove that it was friendly and would help them do their job.

If we did not accomplish this end, our demo would fail. The first task the PM 550 was programmed to perform was tower top temperature.
This was originally set up as shown in Fig. 1. Note tray "x" temperature set the flow of the reflux.

The PM 550 was programmed to take the tray "x" temperature as a process varible (PV) with an operator adjusted set point. The output of this controller was cascaded to programmed flow controller. This arrangement is shown in Fig. 2.

Fig. 1

Original tray "x" control scheme

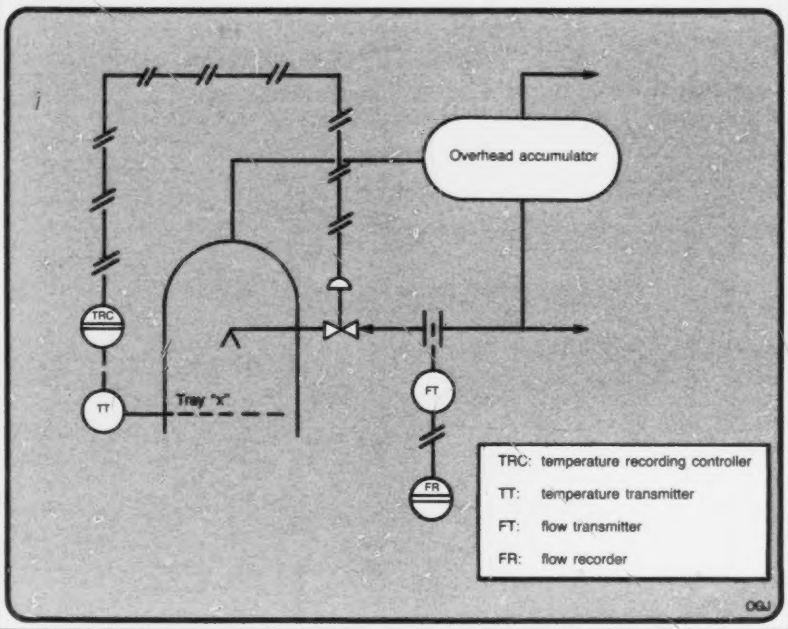
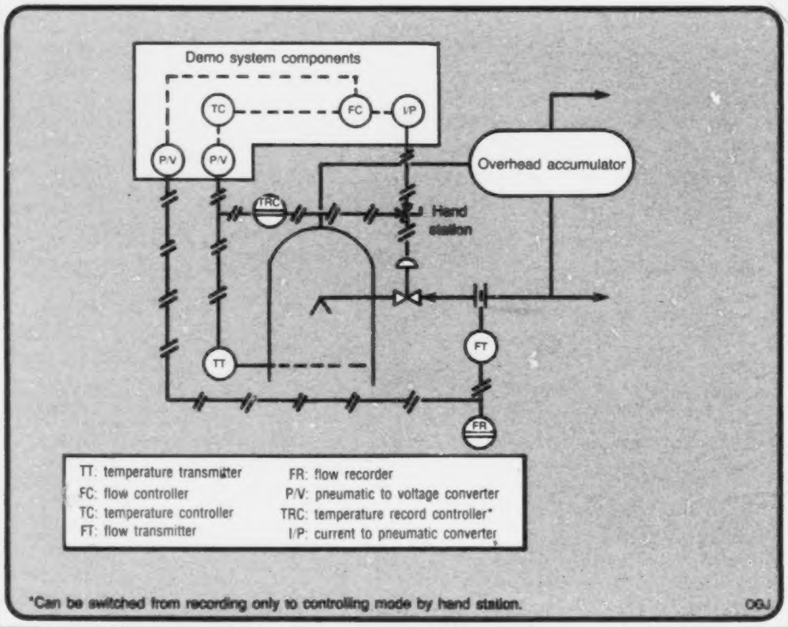

Overhead accumulator
TRC
TT
Tray "x"
FT
FR
TRC: temperature recording controller
TT: temperature transmitter
FT: flow transmitter
FR: flow recorder
OGJ

Fig. 2

Modified tray "x" control scheme


Demo system components
TC
FC
I/P
P/V
P/V
TRC
Hand station
Overhead accumulator
TT
FT
FR
TT: temperature transmitter
FC: flow controller
TC: temperature controller
FT: flow transmitter
FR: flow recorder
P/V: pneumatic to voltage converter
TRC: temperature record controller*
I/P: current to pneumatic converter
OGJ

*Can be switched from recording only to controlling mode by hand station.

There is nothing new in this type of scheme. The operators were a little bit hesitant because of their experiences with cascade control. The PM 550 is truly bumpless, and performed this simple control function well. Operator confidence started to build.

Next we moved into side draw decoupling. This is particularly useful in crude units because in a multiple product tower if a product draw rate is changed, it always affects the next lower product draw rate. In a draw decoupling scheme, the system will automatically adjust the next lower product draw rate in an equal but opposite direction to the changed product draw rate. In our application to three streams, which we chose to decouple, we were successful.

The operators were particularly pleased with the improvement in tower stability with crude rate changes. While we were going after operator acceptance we were searching the literature, programming our spare PM 550, and getting ready for the next step, which was end-point control.

We put the tower on end-point control in early 1983. We ran the CTU for 21 days with no operator mistakes. During this time the laboratory end-point standard deviation was considerably reduced.

The products on control (and decoupling) were light straight run (LSR), naphtha (NAP), kerosine (KERO), and heating oil and distillates (HOD).

In order to do end-point control, the PM 550 was programmed to produce 11 loops, and a microcomputer was added to the system to provide a better operator window. The PM 550 performed all of the mathematics to calculate the product end point, which was based, in part, on mass and energy balances performed on the tower. We used about 80% of the capacity of the machine.

With the 21-day run, we successfully proved to management that advanced control on the CTU was possible. Using this data, and projected energy savings data, the refinery was able to obtain an authorization to upgrade the No. 1 crude topping and crude vacuum unit control system, retaining the existing pneumatic field transmitters.

**The system.** The engineering center and refinery engineers worked together for several months to decide on the best system for the refinery. We decided to:

- Retain the pneumatic panel (as a back up/start-up system).
- Keep as much control as possible in the instrument system.

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Based on a paper presented at the Forty First Annual Symposium on Instrumentation for the Process Industries, Texas A&M University, College Station, Tex., Jan. 21-24, 1986.

- Use a general purpose computer as the process control computer.

This series of decisions resulted in a three-tier control system as shown in Fig. 3.

The truly unique feature in the proposed system was the stand alone general purpose host computer supervising a distributed control system. We did not want the unit operators to have to deal directly with the host computer, nor did we want the system to rely on the host computer for PID algorithms in the form of direct digital control.

The control objectives show that we were truly looking at advanced control for the unit. We do not intend to discuss the control strategy here, but the objectives are:

1. Ratio furnace tube velocity steam-to-charge rate
2. Calculate and alarm furnace efficiencies
3. Control desalter temperature
4. Optimize hot train pass flows
5. Maximize heavy gas-oil production
6. Ratio side draw stripping steam to product rates
7. Control flash-zone temperatures in lieu of transfer
8. Control crude-tower pumparounds on a liquid/vapor basis
9. Control crude-tower product end ponts on a closed loop basis, using calculated inferred values.

Next, we looked at several instrument vendor systems with a mind to our three-tier approach. We found that the Moore Products Co.'s Mycro System offered the best solution. Fig. 4 shows how the information busses are arranged. Fig. 5 shows the final installation.

Fig. 3

Modified controls use three-tier system

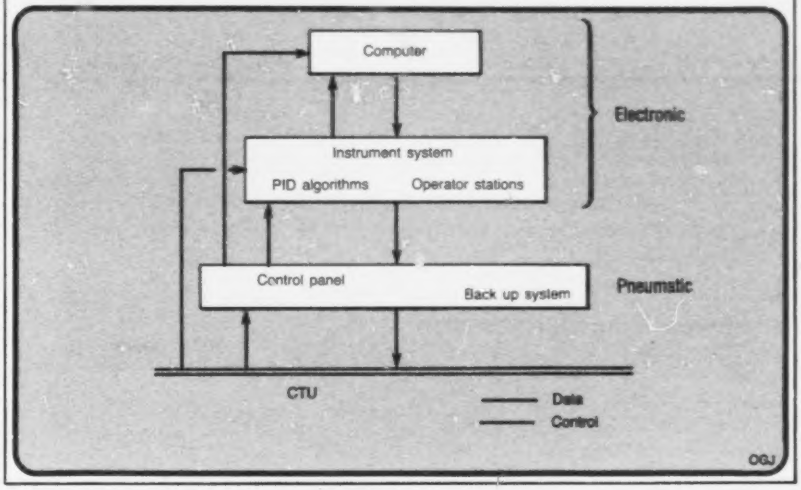

Computer
Instrument system
PID algorithms
Operator stations
Electronic
Control panel
Back up system
Pneumatic
CTU
Data
Control
OGJ

Fig. 4

Standard vendor package

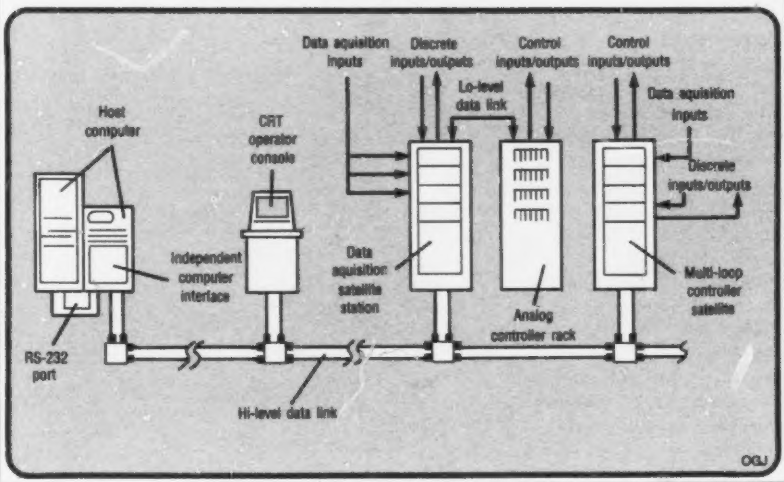
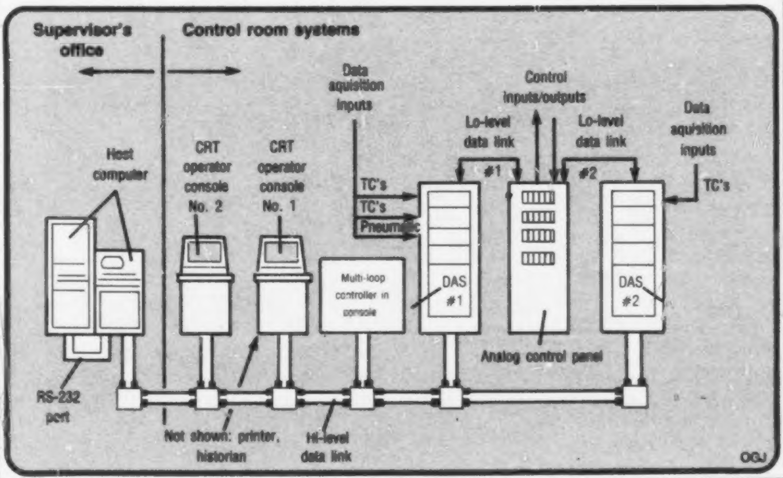

Data aquisition inputs
Discrete inputs/outputs
Control inputs/outputs
Control inputs/outputs
Lo-level data link
Data aquisition inputs
Host computer
CRT operator console
Discrete inputs/outputs
Independent computer interface
Data aquisition satellite station
Multi-loop controller satellite
Analog controller rack
RS-232 port
Hi-level data link
OGJ

Fig. 5

Actual control package on Conoco's crude unit


Supervisor's office
Control room systems
Data aquisition inputs
Control inputs/outputs
Lo-level data link
Lo-level data link
Data aquisition inputs
Host computer
CRT operator console No. 2
CRT operator console No. 1
#1
#2
TC's
TC's
Pneumatic
TC's
Multi-loop controller in console
DAS #1
DAS #2
Analog control panel
RS-232 port
Not shown: printer, historian
Hi-level data link
OGJ

Note that a large number of field inputs are brought into DAS 1, and some inputs are brought into DAS 2. The host computer was placed in the unit supervisor's office, which is adjacent to the control room. The beauty of the general purpose computer becomes apparent when one realizes that the supervisor's office is not a "clean" room.

We took delivery of the system in the fall of 1984 and staged the system in one of our labs. We spent the next several months configuring and debugging the complete system. This would include the console system, its I/O, and the high level computer. We had to made decisions as to which control objectives would go into the high level computer and which objectives would go into the console system.

We placed the furnace velocity steam control and product-to stripping-steam control in the console system. The hot train optimization control was placed in the multiloop controller which is part of the console system. This meant that if we lost the high level computer, the above three control objectives would still function.

The remaining objectives were placed in the multiloop controller (MLC) with set points and/or process variables coming from the high level computer. For example, the product draw would be controlled by a cascade control loop. The inner loop would be a flow controller while the outer loop would be the end point controller.

The Hewlett Packard (HP) computer would calculate inferred end point, send this as the process variable to the end point controller (resident in the MLC), which, in turn, would send a set point to the product draw controller in the panel board. This draw (or flow) controller is a digital set pneumatic controller. The arrangement is shown in Fig. 6.

After we were satisfied with our control system, we used closed loop feedback to check out its control functions. This was done using the high level computer as a crude model to send simulated process signals to itself and the Moore system.

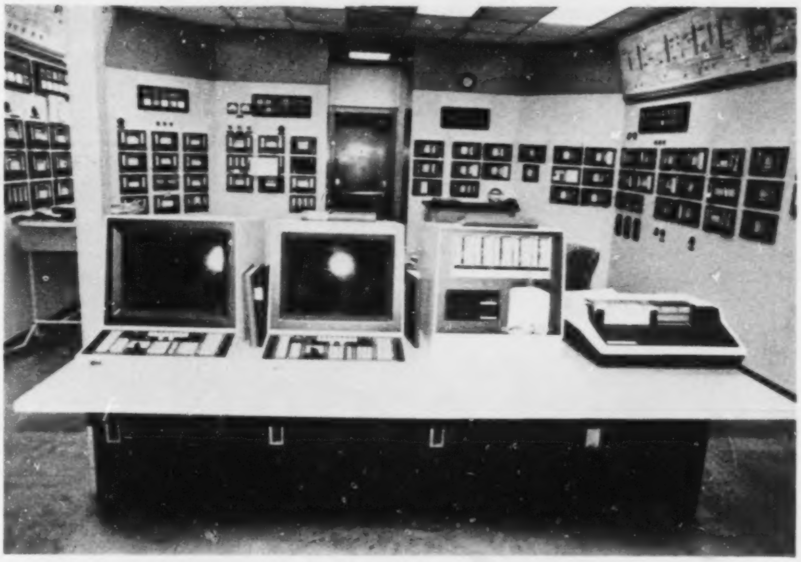
Using this simple technique, we were able to find a number of problems in the vendor's equipment and software, and in our control schemes. Towards the end of this period we were even able to train the operators on the use of the system.

**Training.** We were quite concerned about the operator's acceptance of, and ability to use, the system. All of the operators were required to spend one full day with the unit process engineer using the simulator to find out how the system worked.

The training program went through the use of the distributed control system, the use of the CRT screens, the use of the manual backup panel, the advanced control schemes, and the interaction between the unit and the host computer. Partial and complete failures of the control system were simulated in order to demonstrate what had to be done by the operators.

We felt that the training program was useful, but more good could have been obtained if a second-shorter period prior to start-up had been spent with the operators. This second period would have helped to avoid "cockpit" errors that will be described later.

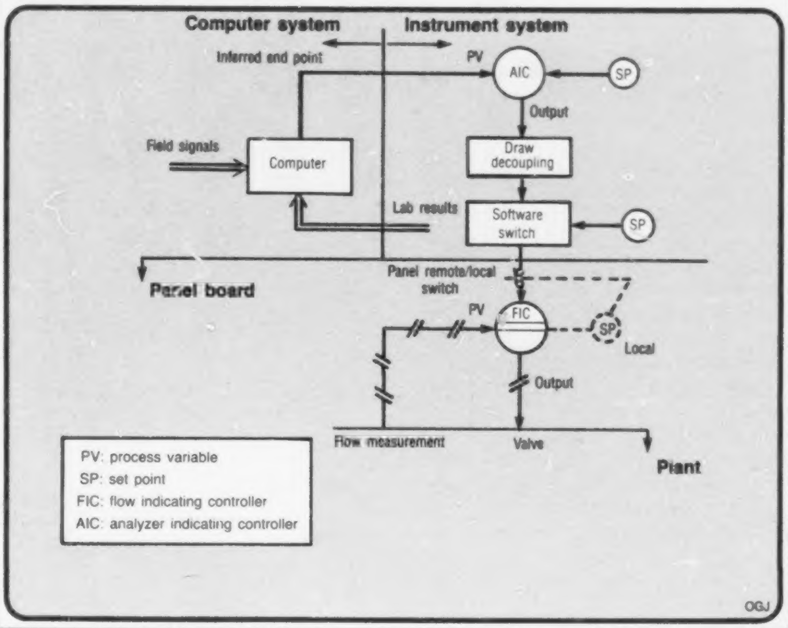
**Documentation.** The problem of documentation always raises its ugly head. We decided at the outset that one team member would be responsible for the system configuration and that another would be responsible for the host computer program.



**Conoco's** crude topping unit control rrom showing the control panel board with the operators' control console in foreground

Fig. 6

Draw flow control scheme

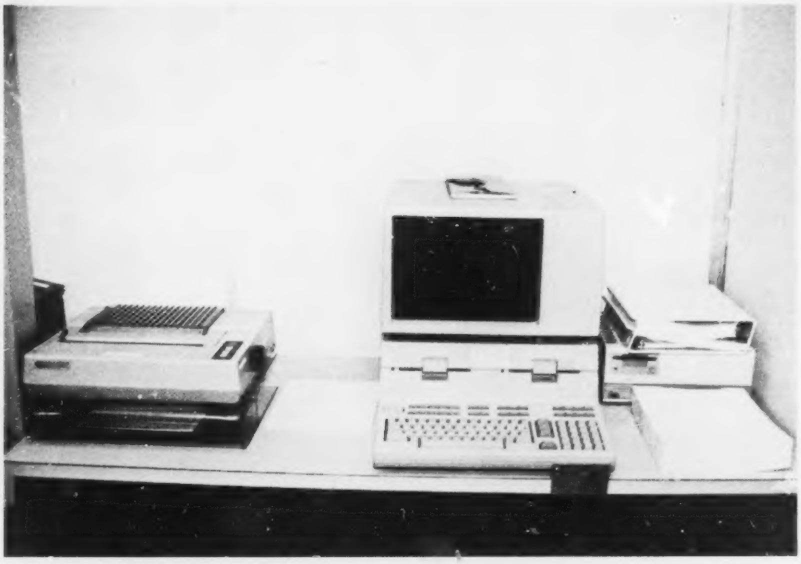


Each member would make certain that all changes would be recorded on the system documents. Any strange programming or configuration techniques would be carefully explained in a supplemental document to be issued when the project was complete.

It is interesting to note that the two supplemental documents used some 200 pages of typewritten material, plus numerous diagrams, etc.

A revision system has been set up where the system documentation recipients will receive updated pages whenever a major system change is made. So far only one such documentation revision has been made. This revision covered all changes made during start up, and minor system changes, such as meter factor corrections, through the middle of November.

The reader should be warned that a simple meter factor change can cause a tremendous volume of paper work. For example, suppose that the naphtha-draw meter factor is changed. This



**The high-level computer** shown is an EP 9836 computer, located in the unit supervisor's office, that provides process variables and set points.

means that the flow controller associated with draw must be rearranged and recorded. The host computer must be informed of the change, and the draw decoupling calculations must be up dated.

**Installation.** The crude unit was scheduled for turnaround in April 1985. In March we started installing some of the new pneumatic controllers in the panel.

This allowed us to debug and tune loops while the unit was still on stream. During the turnaround, we moved the control consoles and computer system into place, completed installation of panel controllers, and awaited start-up.

**Start-up.** The unit was brought on line in late April 1985 using the board-mounted pneumatic controllers. Over the next month, the console system was activated and the operators were slowly introduced to control of their unit (the old way) from the CRT consoles. During upsets the operators would always go back to the pneumatic panel controllers. (We find that a number of them still like to do this!).

After a month or so we placed the side draw decoupling control into service. This was followed by our other advanced control schemes. Nothing was easy, but by late September we had implemented most of our concepts.

We have made minimal changes to the system. We have found that without the benefit of a closed loop simulator, it can be dangerous to make major changes to any of the control schemes.

It is absolutely necessary to have resident experts available to catch problems as they develop in the system. Some of the incidents that occurred caused a number of problems.

Most of these problems are the so-called "cockpit errors." The operators see what they think is a problem and take the system off control.

For example, the hot-train optimization loop became unstable apparently because of a tuning problem. Rather than take this loop off of control, the operator took the whole crude unit off control. He transferred control of the unit from the CRT system to the old pneumatic panel board. We have had numerous similar type events where an operator would transfer back to the old system.

As another example, the LSR end point controller became unstable late last year. This, in turn, also bounced the NAP end point controller.

The refinery personnel were still not fully acquainted with the system, and the crude unit was taken off advanced control. This time the CRT system continued to be used.

The unfortunate situation was that end point control and L/V control of the CTU should have been shut off leaving all other advanced control running.This was not done, and the unit operated for several days before the problem was traced to a suspected (note the use of "suspected") open tower-top temperature TC.

We believe that the intermittent signal caused the LSR end point calculations to bounce, which in turn caused the LSR controller to bounce. Again the lack of training on our part was a major factor in the decision to go off control.

## The authors. . .

**Alworth**

**Evens**

C. W. Alworth is chief consultant for the technical staff of the Conoco Engineering Center in Ponca City, Okla. He is responsible for instrumentation systems for refining, petrochemicals, coal mining, oil production, bulk materials transportation, and marine systems. Alworth's primary experience is with advanced control systems using programmable logic controllers, particularly for safety shut down systems, boiler/burner management, and Conoco's automated decoking system. Prior to joining Conoco in 1974, he taught electrical engineering at the University of Oklahoma, and he was an assistant professor of electrical engineering at Texas A&M University. Alworth has BSEE, MSEE, and PhD degrees from the University of Oklahoma and is a registered professional engineer.

D. A. Evens is senior consultant in the instrument systems division of the Maintenance Engineering Department of Conoco's Engineering Center. He is responsible for the design and development of crude unit advanced control systems and gasoline blender control systems. Evens was a project engineer, responsible for the design of aircraft gas turbine engine controls at Woodward Governor Co. prior to joining Conoco in 1970. He has a BSME from the University of Wisconsin and he is a registered professional engineer.

We, as mentioned in an earlier part of the paper, provide instrumentation services throughout the company. As a part of our service to the refinery we are charged with transferring the software operation to refinery staff engineering. Since the refinery is happy with the system, we are now taking steps to make this transfer.

**Summary.** An old pneumatically controlled plant or process unit can be upgraded to a modern instrumentation system without replacing existing pneumatic transmitters and control elements.

### Acknowledgment

Thanks to the Ponca City refinery technical services staff, without whom the idea would never have started nor been completed. Also, the encouragement and patience of the operators and instrument/electrical staff in the refinery is appreciated. Finally, we appreciate the help from Moore Products Co. for the use of some of its material. ▪

# Flare-stack sizing calculations

**Tom C. Tsai**
TDS Associates
Houston

Sizing of flare stacks can be programmed on a microcomputer using both the API method and a new procedure that incorporates flame-shape and flame-length models.

The industrial standard practice of flare-stack sizing follows the procedures outlined in the American Petroleum Institute (API) standard RP-521.[1] Recently, an alternate procedure has been proposed by others.[2] This new procedure incorporates a new prediction model of flame shapes and flame lengths.

Both the API standard and the new procedure can be programmed for solution on a microcomputer. The programmed solutions will expedite the tedious calculations and improve the accuracy and consistency of flare-stack sizing.

A comparison of the two methods is made by presenting the results of their use along with the results of other methods available in the literature. And experimental data of flame length vs. heat release is correlated.

To assist the reader in writing a program for the methods, an algorithm and working equations are presented, and example problems are illustrated.

**Technical background.** A quite comprehensive design guideline for a flare stack has been well documented in API RP-521. This set of guidelines has been closely followed by engineering designers practicing flare-stack sizing and other disposal system designs. Detailed procedures and associated design considerations of the guidelines are documented in Section 4, "Selection of disposal systems," in API RP-521. This method is hereafter referred to as Method A.

Recently, Oenbring and Sifferman conducted some tests based on actual plant data.[2] Their results indicated that the point-source approach to flare calculations was adequate.

They also recommended new F factors for various emitting gases and adopted the Brzustowski's model for predicting flame shapes and flame lengths.[3] New values of allowable thermal radiation heat fluxes were suggested.

These values are more aggressive than the values given in API RP-521. The method proposed by Oenbring and Sifferman is hereafter denoted as Method C.

One other method available in the literature includes some parameters not used in these two methods.[4] For example, pressure drop across the flare tip was employed to carry out a number of calculations for comparison. Based on the analysis and results of this study, certain design criteria and good design practice are recommended.

**Programming aids.** The algorithm of the program is presented in Fig. 1. Inputs to the program are: flaring gas flow rate, molecular weight of the gas, the gross heat of combustion, temperature, and ratio of specific heats of the gas (Cp/Cv).

**Determination of stack diameter.** The first calculation required for a program is to determine the flare-stack diameter. As indicated in Fig. 1, three options are available.

The user has the option of calculating the diameter based on a given Mach number (Option M, Fig. 1), or calculating the Mach number based on a trial diameter (Option D, Fig. 1). If help is needed on how the program calculates the Mach number and stack diameter, the user can invoke a help command (Option H) to display the helping messages on the screen. This creates a user-friendly feature for the program.

If the user selects the D option, the computer will first ask if the user wants the explanation of Mach number. If the answer is yes, the computer then displays information on the usage of Mach number and provides the various suggested criteria on Mach number.

If the answer is no, the computer will request an input of the trial diameter.

The computer then calculates the sonic velocity, Vs, in feet per second using the following equation:

$$Vs = 223\ (kT/MW)^{0.5} \qquad (1)$$

# can be programmed on a microcomputer

Table 1

## Comparison of API-521 and Oenbring/Sifferman methods

| Item | API-521 | | Oenbring/Sifferman | |
|---|---|---|---|---|
| Flare-stack diameter | Basically the same for both methods | | | |
| F-factor (fraction of heat radiated) | 0.20 for methane<br>0.30 for heavier gas | | 0.25 for 16.8 MW gas<br>0.40 for 40 MW gas with steam<br>0.50 for 40 MW gas w/o steam | |
| | **Heat flux** | **Time** | **Heat flux** | **Time** |
| Allowable flux for personnel exposure (heat flux in BTU/hr-sq ft) | 440<br>740<br>2,200 | Infinite<br>40 sec<br>9 sec | 600<br>1,100<br>2,000 | Infinite<br>5-10 min<br>15 sec |
| Flame length and deflection | Procedures described in Sec. 4 with example illustrated in Appendix B of API RP-521 | | Recommended adoption of Brzustowski's model for predicting flame shapes and length | |

where:

$V_s$ = Sonic velocity, fps
k = Ratio of specific heat at temperature, Cp/Cv
T = Temperature, °R.
MW = Molecular weight of flaring gas, lbm/lb-mole

The actual cubic feet per second is calculated as follows:

$$\text{acfs} = (\text{scfs})(T)/(1.872 \times 10^6) \quad (2)$$

where:

scfs = Flow rate in standard cu ft/sec
acfs = Flow rate in actual cu ft/sec

The gas exit velocity, Ve, in feet per second is calculated by:

$$Ve = \text{acfs}/(\pi D^2/4) \quad (3)$$

where:

Ve = Gas exit velocity, fps
D = The stack diameter, ft

The Mach number is then calculated by:

$$\text{Mach number} = Ve/Vs \quad (4)$$

A Mach number of 0.7 is recommended as the design criterion for maximum gas exiting velocity. If the calculated Mach number is over 0.7, a warning message should be displayed to alert the user.

If the calculated Mach number is less than 0.7, the calculated Mach number should be displayed, and a prompt should be displayed by the computer, asking the user whether another diameter is to be tried. If the answer is yes, the user will be prompted for another input trial diameter, and the above procedures are repeated until a calculated Mach number is satisfactory to the user.

Once a satisfactory diameter is determined, the next step is to calculate the stack height.

If the user chooses Option M, the program will follow the procedures indicated in the right-hand portion of Fig. 1. Again, the computer will ask the user whether there is need of an explanation about the Mach number.

Information about Mach number will be displayed if the answer is yes. Otherwise, the computer will prompt the user for inputing the Mach number. It then proceeds to calculate the sonic velocity, the actual cubic feet per second of the emiting gas, and the stack diameter.

The user has the opportunity at this time to input another Mach number and, consequently, to calculate another diameter if desired. Once the user is satisfied with the results of the stack diameter, the computer then proceeds to calculate the stack height.

**Determination of stack height.** It should be noted that both Method A and Method C are the same as far as the determination of flare-stack diameter is concerned. As indicated in Fig. 1, the user has three options after the stack diameter is determined. The user can choose Method A, Method C, or request an explanation for both methods.

For Method A, the user is prompted for inputting the ground distance from flare base to the point of interest, the F-factor, and the maximum allowable radiation intensity. The user has the option to enter the wind velocity if desired.

If the wind velocity is provided, the computer then determines the effect of wind velocity on flame lengths and flame shapes.

The distance required between atmospheric venting and point of exposure where thermal radiation must be limited is determined by:

$$DR = [FQ/(4\pi k)]^{0.5} \quad (5)$$

where:

DR = Minimum distance from midpoint of the flame to the object being considered, ft
F = Fraction of heat radiated, dimensionless
Q = Heat released, BTU/hr
K = Allowable radiation, BTU/hr-sq ft

The calculated distance, DR, from Equation 5 is based on a vertical flame burning in still air. Flame under the influence of wind will tilt in the direction the wind is blowing. Hence, a correction should be applied to take the flame length into account since all radiation is considered to emanate from the flame midpoint.

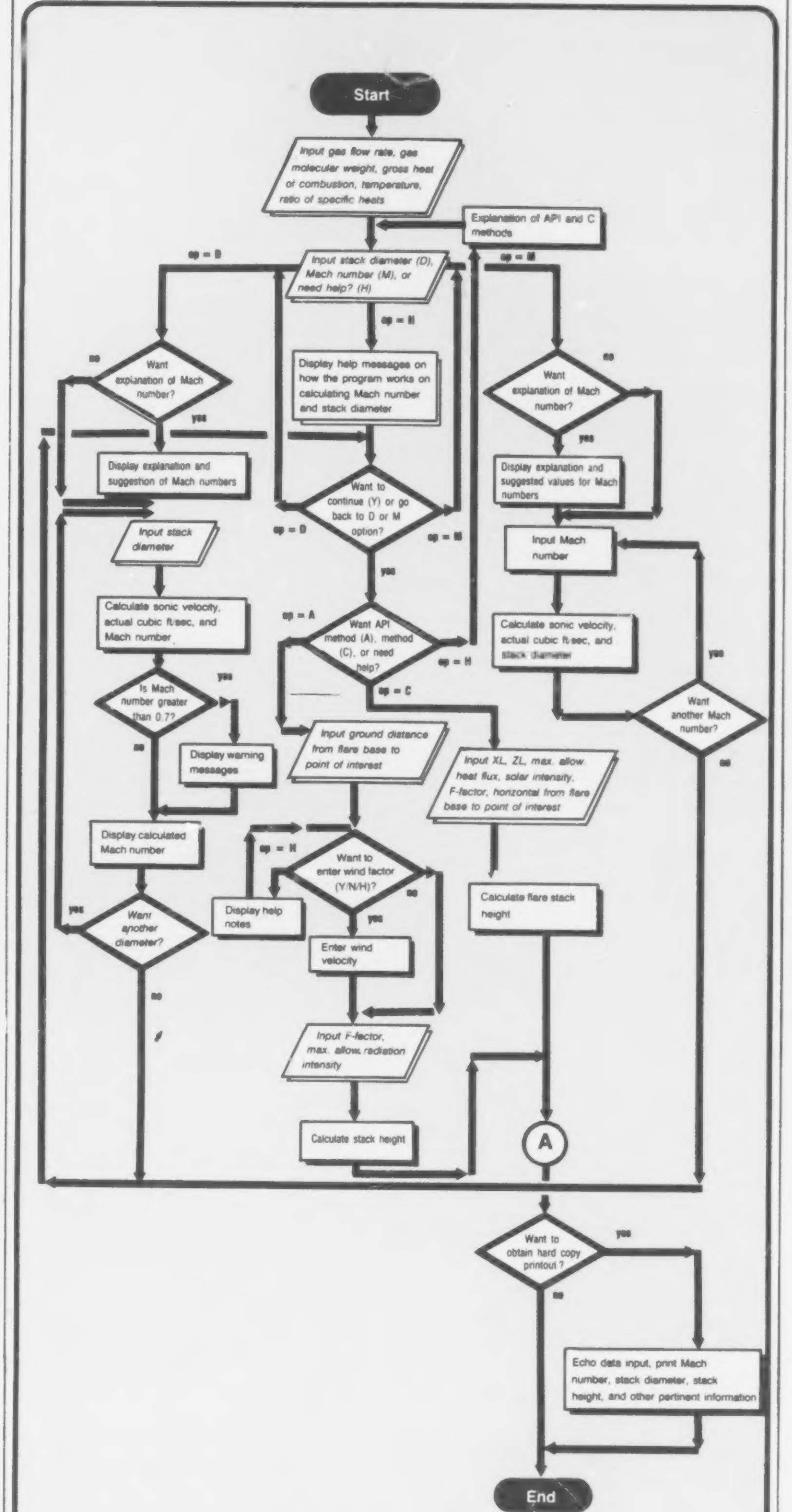
Some plant-scale data on flame lengths are shown in Fig. 4 of Section 4, API RP-521. These data are correlated by regressional analysis as shown below and used in the program:

$$DM = 0.4675\ (\ln(Q)/2.3026) - 2.12 \quad (6)$$

$$FL = (10)^{DM} \quad (7)$$

Fig. 1

## Algorithm for programming flare-stack calculations


Start
Input gas flow rate, gas molecular weight, gross heat of combustion, temperature, ratio of specific heats
Explanation of API and C methods
Input stack diameter (D), Mach number (M), or need help? (H)
op = D
op = H
op = M
Display help messages on how the program works on calculating Mach number and stack diameter
Want explanation of Mach number?
no
yes
Display explanation and suggestion of Mach numbers
Want to continue (Y) or go back to D or M option?
op = D
op = M
yes
Want explanation of Mach number?
no
yes
Display explanation and suggested values for Mach numbers
Input Mach number
Calculate sonic velocity, actual cubic ft/sec, and stack diameter
Want another Mach number?
yes
no
Input stack diameter
Calculate sonic velocity, actual cubic ft/sec, and Mach number
Is Mach number greater than 0.7?
yes
no
Display warning messages
Display calculated Mach number
Want another diameter?
yes
no
op = A
Want API method (A), method (C), or need help?
op = H
op = C
Input ground distance from flare base to point of interest
Input XL, ZL, max. allow heat flux, solar intensity, F-factor, horizontal from flare base to point of interest
op = H
Want to enter wind factor (Y/N/H)?
no
yes
Display help notes
Enter wind velocity
Input F-factor, max. allow. radiation intensity
Calculate stack height
Calculate flare stack height
A
Want to obtain hard copy printout?
yes
no
Echo data input, print Mach number, stack diameter, stack height, and other pertinent information
End

OGJ

where:

Q = Heat released, BTU/hr
FL = Flame length, ft
DM = Dummy variable

The effect of flame distortion due to lateral wind on the jet velocity from a flare stack follows the procedures outlined in Fig. 5, Section 4, of API RP-521.

Calculations of flame distortion are accomplished by an iterative loop in the program. Ten iterations were found to be sufficient for obtaining reasonable accuracy. In case the calculated flare-stack height is less than 100 ft, a statement should be inserted that indicates the recommended minimum design flare-stack height is 100 ft.

For Method C, the user is prompted to input XL, ZL, maximum allowable heat flux, solar intensity, F-factor, and the horizontal distance from flare base to the point of interest. XL is the distance downward from the center of the discharge jet, and ZL is the vertical distance above the flare tip.

XL and ZL are calculated based on the Brzustowski's model for predicting flame lengths and flame shapes.[3] The information required for Brzustowski's model are: flare-gas molecular weight, flare-gas density at tip, flare-gas discharge velocity, tip inside diameter, wind velocity, density of ambient air, molecular weight of air, and gas composition in mole fractions.

The program proceeds to calculate the distance, DR, from the flame center point to the point of maximum allowable intensity using Equation 5. Different values of F factors are recommended by Oenbring/Sifferman.

The K values used here, however, are obtained by subtracting the solar radiation intensity from the total allowable heat flux. This is different from the API method in which values of the total allowable heat-flux intensity are used in Equation 5. Q is the total heat released in BTU per hour.

With the DR values determined and the horizontal distance from base of stack to the point of allowable radiation intensity inputed, the flare-stack heights are calculated. Again, a minimum 100 ft of flare-stack height is recommended if the calculated height is less than 100 ft.

Although the wind velocity is not explicitly requested in the procedures shown in Fig. 1 for Method C, the effect of wind velocity is included in the calculations of XL and ZL.

Upon completing the calculations of stack height, a prompt is displayed requesting whether a hard copy is desired. If so, the computer echos the input data and prints the calculated

Table 2

## Typical output for example problem using API RP-521

```
This program calculates flare-stack diameter and height:
Echo of input data:
   Gas flowrate, lb/hr                                              = 10,000
   Gas molecular weight                                             = 46.1
   Gas gross heat of combustion (LHV)*, BTU/lb                      = 21,500
   Gas temperature, °F.                                             = 300
   Ratio of specific heats, k of the gas, (Cp/Cv)                   = 1.1

Calculated results on stack diameter:
   Sonic velocity for the flared gas, fps                           = 949.43
   Gas exit velocity, fps                                           = 189.89
   Actual volume flow rate at tip, cfs                              = 334.06
   Mach number                                                      = 0.2

Flare-stack diameter, ft                                            = 1.5
Calculated flare stack height by API RP-521 method:
   Heat content of gas, BTU/hr                                      = 2.15 E+09
   Ground distance from flare to point of interest, ft              = 150
   Design wind velocity, mph .                                      = 20
   F-fraction of heat radiated                                      = 0.3
   Max. allow. radiation at point of interest, BTU/hr-sq ft         = 2,000

   Flare stack height by API method, ft                             = 78.87

Note: Design flare stack for minimum height of 100 ft.
```

*Lower heating value

Table 3

## Method C example problem results

```
This program calculates flare-stack diameter and height:

Echo of input data:
   Gas flow rate, lb/hr                                             = 59,842
   Gas molecular weight                                             =     16.8
   Gas gross heat of combustion (LHV)*, BTU/lb                      = 20,850
   Gas temperature, °F.                                             =     46
   Ratio of specific heat k of the gas, (Cp/Cv)                     =      1.31

Calculated results on stack diameter:
   Sonic velocity for the flared gas, fps                           = 1,398.69
   Gas exit velocity, fps                                           =   279.74
   Actual volume flow rate at tip, cfs                              =   365.15
   Mach number                                                      =     0.2

   Flare stack diameter, ft                                         =      1.29

Calculated stack height by Oenbring/Sifferman method:
   Flame length and deflection by Brzustowski's method, XL, ft      =   28.2
   Flame length and deflection by Brzustowski's method, ZL, ft      =   72.7
   Max. total allow. heat flux at point of interest, BTU/hr-sq ft   =  600
   Solar radiation intensity assumed, BTU/hr-sq ft                  =  350
   F-fraction of heat radiated                                      =    0.25
   Horizontal distance from flare base to point of interest, ft     =  200

   Required flare stack height by Oenbring/Sifferman method, ft     =  218.07
```

*Lower heating value

Mach number, the stack diameter, the stack height, and other pertinent information.

### Methods compared

A comparison between API RP-521 and the Oenbring/Sifferman method is summarized in Table 1. As mentioned earlier, both methods are the same for determining the flare-stack diameter.

Three main categories of difference in calculating the flare-stack heights are: F-factors (fraction of heat released) recommended, allowable heat flux for personnel exposure, and calculation of flame lengths and flame shapes.

**Example problems.** Tables 2 and 3 illustrate the format of a typical computer printout. The example problem in Table 2 shows the results by the API method. It should be noted that the calculated flare-stack height is less than 100 ft and, hence, a statement indicates the recommended minimum height is 100 feet. Table 3 shows the results of another case using the Oenbring/Sifferman method.

**Other methods.** Comparison of results predicted by a program with the results calculated by the methods of certain vendors available in the literature indicates great variations in the final stack sizes.[4]

These variations arise from the differences in the pressure drops allowable, the fraction of radiation heat release emissivity, the coordinates of flame center, and the allowable radiation heat flux.

A microcomputer program capable of calculating the flare-stack diameter and flare-stack height can be written from the information presented. All of the necessary equations and formulas required are listed, and various design criteria are suggested. Hence, the program can be used for the preliminary design of a flare stack, or it can be used for optimizing the flare-stack sizing.

Great variations in results among the various methods exist. Therefore, it is recommended that each flare application be individually evaluated. The user is urged to check with the flare tip vendors to ensure that the design Mach number is consistent with the vendors' specifications.

Both the API and Oenbring/Sifferman methods can be incorporated into a program. Although the API method is conservative in the thermal radiation for personnel exposure, it does not necessarily lead to a more conservative design in flare-stack height.

Therefore, both methods should be evaluated individually based on actual process conditions.

It is ultimately the user's decision and responsibility to come up with a final design which best suits the system requirements.

## The author. . .

Tsai

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3. Brzustowski, T.A., "A Model for Predicting the Shapes and Lengths of Turbulent Diffusion Flames Over an Elevated Industrial Flare," 22nd Canadian Chemical Engineering Conference, Toronto, 1972.
4. Straitz, J.F. III, "Nomogram Determines Proper Flare-tip Diameter and Flare Stack Height," Oil, Gas & Petrochemical Equipment, July and August 1979.

# Mossmorran NGL fractionation plant has

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The new Mossmorran NGL fractionation plant in the U.K. has a computer-based operation and control system.

The Mossmorran facility is part of the Far North Liquids and Associated Gas System (Flags) operated by Shell U.K. Exploration & Production (Shell Expro) on behalf of the Shell/Esso joint venture.

Shell Expro's Flags project (Fig. 1) comprises the under-sea pipeline from the North Sea oil fields to St. Fergus, the St. Fergus separation plant, the connecting land pipeline to Mossmorran, the Mossmorran fractionation plant and the shipping terminal at Braefoot Bay.

At St. Fergus, the methane and some ethane are removed and sold to the British Gas Corp. for distribution in the national natural gas transmission network. The balance of the associated gas consists of ethane, propane, butane and condensate.

**Mossmorran plant.** NGLs are transported to Mossmorran as a liquid by pipeline and fractionated into separate components.

Ethane will primarily be used as feedstock for an ethylene plant also located at Mossmorran. A small quantity may also be used as NGL plant fuel.

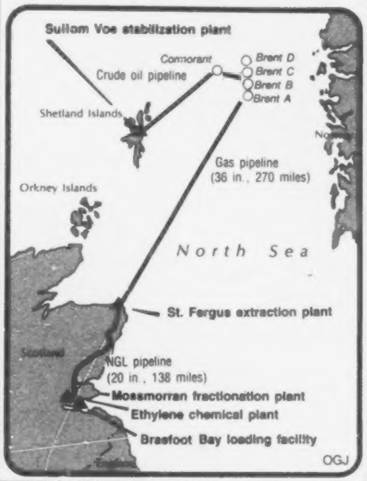
Propane and butane are stored separately on site in special low temperature tanks. These products are dispatched by seagoing tankers. Condensate is also sold separately and dispatched by ship.

The shipping terminal, Braefoot Bay, is linked to Mossmorran by underground pipelines.

Fractionation is performed in two parallel trains (Fig. 2), each consisting of a deethanizer, a depropanizer, and a debutanizer. The reboil heat is supplied by hot oil systems. Compressors supply propane refrigeration for condensing reflux on the deethanizers, liquefying product, and condensing tank boil-off.

Fig. 1

Flags project



The long (138 miles) pipeline from St. Fergus and the absence of any intermediate storage means that the Mossmorran operation must be closely coordinated with that at St. Fergus. Since there are no storage facilities for off-specification products, the operation at Mossmorran must also be closely controlled.

**Instrumentation.** The need for high reliability and efficient, safe operation convinced Shell engineers that a modern automated instrument system should be installed.

A microprocessor-based process control and data acquisition system (Honeywell's TDC-2000) performs most of the functions of conventional analog instrumentation. In addition, it enables the operator to supervise and control the process from centralized consoles.

Critical alarms, emergency controls and selected status items are hard wired to the control panel. The indications for specialized instruments such as tank gauges, multipoint temperature, fiscal meters, and quality control chromatographs are also on the control panel, in some cases in an abridged form. Shell Expro developed the initial concepts for the computer system, then contracted potential suppliers to develop individual competitive detailed design studies. As a result of these studies, Applied Automation Inc. was selected as the vendor.

Table 1

Project timetable

| | Completed |
|---|---|
| Financial justification | Aug. 1980 |
| Requirements analysis | May 1981 |
| Evaluation of bid list | May 1981 |
| Tender for detailed design study | Sept. 1981 |
| Detailed design studies completed | Oct. 1982 |
| Evaluation of design studies | Dec. 1982 |
| Let implementation contract | Mar. 1983 |
| Factory acceptance in Bartlesville | Feb. 1984 |
| Start-up of system at Mossmorran | Mar. 1984 |
| Plant start-up | May 1984 |
| Phase 1 acceptance complete | Oct. 1984 |

Although the TDC-2000 system provided control capabilities, additional features and capabilities were needed. Put simply, a means was needed to bring all the instrumentation together into one common display interface and, in view of the operating constraints, supervisory control. The Mossmorran operation and control system (MOCS) was installed to meet these needs.

The MOCS greatly facilitates operation of the Mossmorran plant. Under stable plant conditions the control and monitoring facilities will allow safe operation by one operator. During loading of ships or during module start-up and shutdown a second operator will be in attendance.

Information is presented to the operators in a format that is of direct and identifiable use. The console permits access to the TDC operator stations on both data transmission segments (hiways), closed circuit TV, in-plant and off-plant radio systems, and telephone links.

Operational requirements of the system include:

- Enhancement of information presented to operators and shift supervisors so that day to day plant operation and safety are improved. These enhancements include: Color graphics, flexibility in grouping variables in displays, capability to include additional instruments, flexible performance logs, calculated display variables, keyed alarm displays, easily configured trends, and excursion and shutdown reports.
- Computer control/optimization of plant variables to achieve improved economic operation.

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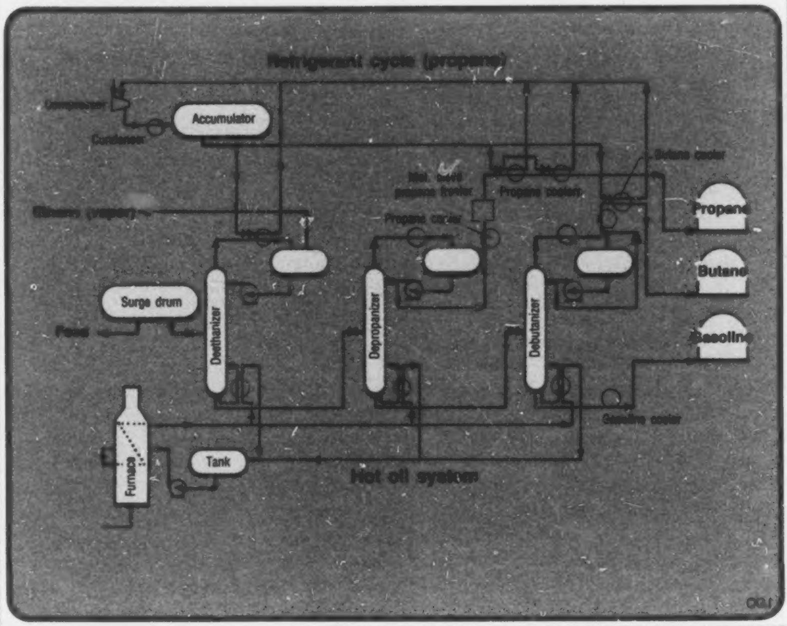
Based on a presentation made at the 64th annual Gas Processors Association meeting, Houston, March 18-20, 1985.

# computer-based operation and control system

Fig. 2

Mossmorran flow scheme



- Provision of a management and technical information system for improved planning and longer term operation of the plant.
- Engineering the computer facilities such that the plant can be satisfactorily controled with the basic instrumentation in the event of a MOCS outage.

**Interfacing.** The MOCS is based on Applied Automation's Optrol 7000 system using PROFORM software. The system interfaces the TDC-2000 data hiways, enabling the MOCS to receive information from the hiways and send commands to the process via these hiways. The MOCS also interfaces to instruments via RS-232, 20 mA current loop, and a programmable logic controller (PLC).

The Optrol 7000 process operator consoles (POC) present information from all these sources to the operator in a single consistent format. Without the MOCS the operator would be faced with a variety of disparate interfaces. The information processing capabilities of the MOCS are shown in Fig. 3.

The MOCS design emphasizes reliability. For this reason the on-line OPTROL 7000 system is backed up by a second, standby, system during normal operations. All critical interfaces are duplicated and frequent file transfers keep the standby machine up to date. The standby system is available for development, investigating plant upsets, and running the plant model.

**System hardware.** The MOCS includes two Perkin-Elmer machines, each comprising a Model 3252 central processing unit (CPU), with 4 megabytes of MOS memory and two disc drives. A line printer is connected to the on-line machine Also included is a dual General Electric PLC with automatic switchover capabilities.

The system configuration provides switchover for all peripheral devices which are necessary for control by the on-line machine. Critical peripheral devices are duplicated to avoid the loss of capability on failure, or because duplication allows for a simpler system.

Both CPUs are linked via a serial RS-232 channel, which supports file transfers between machines for development purposes, etc., at 19.2 kilobaud. In addition, the CPU's are linked via the Perkin-Elmer processor-to-processor interface for high-speed transfer of critical data files. This minimizes data loss in the event of a disc or CPU failure by updating the data files on the standby machine every three minutes.

Both machines have battery backup, power fail/auto-restart. The two disc drives give each machine a total capacity of 128 megabytes of storage. Thirty-two megabytes of this is on removable disc packs and the rest is on sealed units.

A nine track, error correcting magnetic tape drive supports off-line information storage and microfiching. The magnetic tape is switchable between machines.

The on-line and standby CPUs are each interfaced to the TDC-2000 system through dedicated general purpose computer interfaces (GPCI). The OPTROL 7000 functions as a preferred access device on the TDC-2000 hiway. It has the same privileges as a Honeywell basic operator station.

Each machine has a dedicated system console, a typer, an OPTROL 380 POC, and a Perkin Elmer multi-terminal-monitor (MTM) development terminal. In addition to the standard CPU, each machine is configured within a loader storage unit (LSU),a universal clock board and clock and watchdog board.

The system includes a dual General Electric Series 6000 PLC, itself controlled by GE redundant processor unit. This can determine if either of the PLCs are malfunctioning and ensure by means of change-over switching that the good device is connected to the on-line machine.

The PLC supports its own dedicated event typer for back-up operations. The PLC functions as the MOCS interface to alarms and digital status information as well as tank gauges and multiplexed temperature indicators.

The system also includes a buss switch and associated switched chassis. The switched chassis contains controller boards to serially interface to operational typers, main control panel POC's, and data input MTM terminals. The switched chassis contains dual serial interfaces to the chromatograph analyzers and the custody transfer meters. The magnetic tape unit which is independently switched is also included in this chassis.

Multiplexors and modems are provided for remote links to the Mossmorran laboratory and Braefoot Bay shipping terminal. A video hard copy device is connected through a coaxial switch to any one of the POC's.

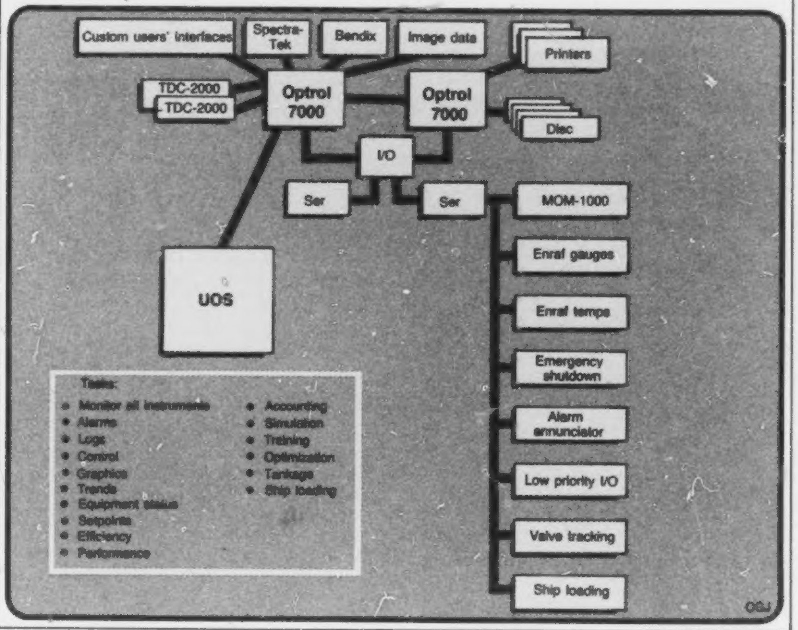


Fig. 3

Integrated plant information

**System software.** The MOCS utilizes standard PROFORM software. This software provides area and unit displays, alarming, dynamic trending, semi-graphics, data acquisition, support of the data base and logs. Also provided is the capability for on-line program alteration, modification, and addition.

Custom software was written for the GE programmable logic controller. The PLC scans and time tags alarms to 0.1 sec accuracy and low priority status inputs every 3 sec. It also scans the coded tank gauge, levels and temperatures, and the multi-point temperature instrument.

Other custom programs generate management information reports, excursion reports, and report instrument status. They also prepare emergency shutdown and preshutdown logs and schedule reminder messages to plant personnel on a daily basis.

Individual reports and supporting programs generally use the actual number of hours involved to produce accumulated sums and time averages. For this reason, a custom program adjusts the number of hours/day, changes the internal clock, and resynchronizes all timed programs to account for seasonal time changes.

**Supervisory control.** The MOCS provides supervisory set point control based on an optimization of the operation. The supervisory set point control functions are designed to control the product specifications at the set points by reference to the on-line quality measuring instruments. The model-optimizer package is run periodically in background on either the on-line or standby machine.

The supervisory control also minimizes plant disturbances by feed forward control. The operator decides on the use of specifications produced by the model. The supervisory controls for the two modules are identical.

The supervisory control functions on the fractionators comprise:

- Composition control on the top and bottom of all columns.
- Minimization of column pressure on the depropanizers and debutanizers within operating constraints to reduce utility costs.
- Non-linear level control on the deethanizer and depropanizer bottoms to reduce disturbances.
- Feed forward adjustment on hot oil flow to compensate for feed rate changes.
- Inclusion of a reflux bias to reduce interaction of the double ended composition control.
- Tray temperature set point control utilizing column pressure and analyzer setpoint in the event of failure of a bottoms analyzer.

The supervisory control functions for the hot oil system comprise:

- Minimization of the hot oil temperature.
- Reduction of interaction between reboiler flow controllers.
- Minimization of flow through the hot oil bypass.

The operation of these strategies with valve position, flow rate, and temperature constraints yields safer operation and maximizes hot oil flow through the reboilers for maximum heat transfer and more efficient furnace operation.

**Model-optimizer.** The model-optimizer helps minimize energy costs and maximizes profits while maintaining products within contractual specifications by providing information to operators. The model-optimizer is a modular program which can simulate and optimize either a single train or the entire plant. The plant configuration, product specifications or constraints can be easily changed without recoding or recompiling the program.

The optimizer is a sectionally linearizing mixed integer linear program. By repeatedly executing the model the optimizer will find the best feasible economic operating conditions and output these to the operator. The model-optimizer can be run, using existing plant conditions, by the operator. It may also be used by the engineer to run case studies for planning purposes.

**Plant installation.** A key objective for the MOCS project was to have the basic data acquisition and display facilities available for plant start-up. The operating personnel were able to familiarize themselves with the use of the MOCS from the beginning and avoid having to change operating practices.

Insofar as possible, Applied Automation provided proven equipment and pre-written software to minizmize the development risk.

A tight schedule was established for the project (Table 1). This schedule was met. As of mid-December 1984 the project was on time, to budget, and meets or exceeds design specifications. Acceptance by all personnel has been higher than could have reasonably been expected. Two of the main reasons for this are:

- The operations department was involved at all times, from the requirements and specification stage right through to installation.
- Most of the key elements of the system were available during the plant commissioning period. Moreover, all functions which were "special to project" were fully tested before release to operations.

The semi-graphics and trending functions have already proved their worth. The use of the PLC interface for time tagging alarms has been invaluable for the analysis of plant trips during the start-up phase.

Substantial progress is being made on the implementation of the supervisory control and model-optimizer functions.

System availablility has been better than 99.5%. ▪

# Octane squeeze won't support capital investments

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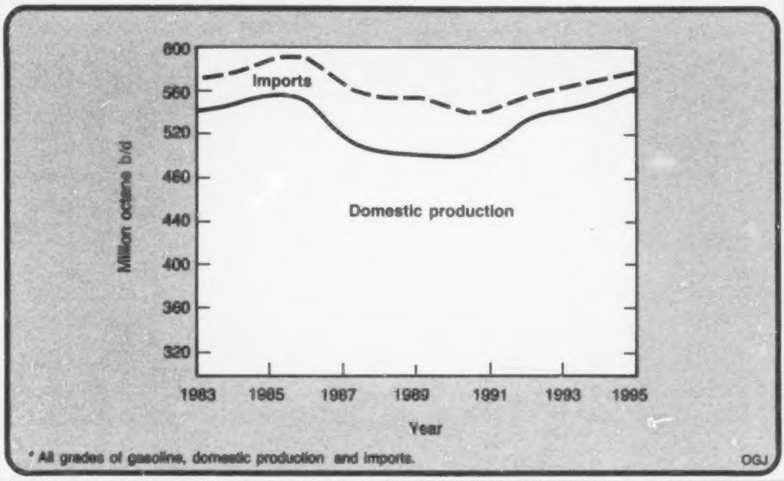
Capital investment in octane upgrading equipment may not meet economic payout requirements if units are not in place and operating by the first quarter of this year. This is revealed by an analysis of the U.S. refining industry and the Environmental Protection Agency (EPA) lead phasedown program.

The octane shortage created by lead phasedown will be temporary because more-efficient cars will replace less-efficient models. As a result, overall gasoline octane demand, based on car fleet changes, will peak in 1986 (Fig. 1).

Also, the analysis shows that the production cost of leaded regular gasoline will exceed the cost of unleaded regular once the lead credits, made available by EPA's lead banking rules, are used up.

Fig. 1

Gasoline octane demand will peak in 1986*



* All grades of gasoline, domestic production and imports.

**Short term.** Shortages in octane are expected in 1986. Any octane shortage that cannot be met domestically must be made up by imports of gasoline, most likely from Europe.

The shortage can be made up by the following methods:

- Reduce unleaded premium production and increase imports.
- Reduce crude-oil runs and increase gasoline imports.
- Use oxygenates and isomerates.
- Maximize use of light-straight-run naphtha to olefin crackers.
- Produce a subgrade leaded and unleaded regular.
- Use banked lead credits.

Of these options, the first two are not economically attractive. Alternative octane improving processes, such as isomerization to upgrade light-straight-run (LSR) naphtha, have been touted as the most logical choice.

Others have viewed investments in oxygenates such as MTBE as the best alternative. However, using oxygenates and isomerates on an industry-wide basis is limited by production capacity and vapor pressure and distillation characteristics. Economic justification of further capacity is not warranted. The viable noncapital alternatives are the last three choices. These options are reviewed and analyzed with some general comments on the refining industry and some implications of lead phasedown.

**Refining uncertainty.** The U.S. refining and related industries face a continuing period of uncertainty. Declining refined product demands, over capacity, and falling crude oil prices have contributed to reduced profits in recent years. A worldwide economic recession, greater energy efficiency, and continued substitution of coal,

Fig. 2

U.S. finished motor gasoline imports

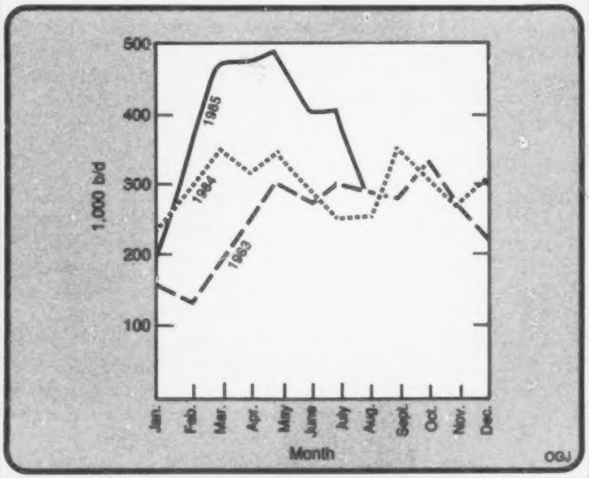


Fig. 3

Paraffinic stocks will be less desirable

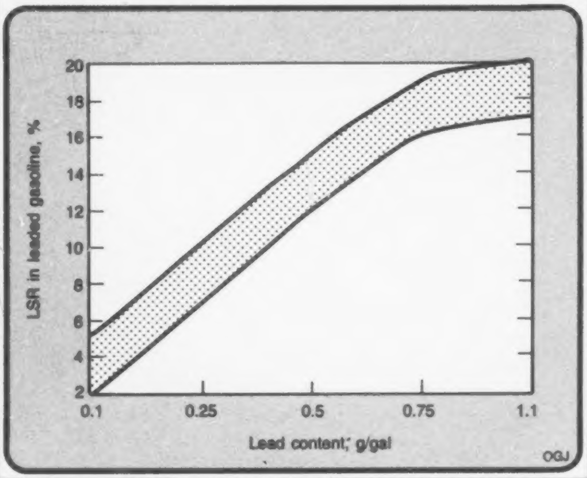


Fig. 4

Marginal octane costs increase

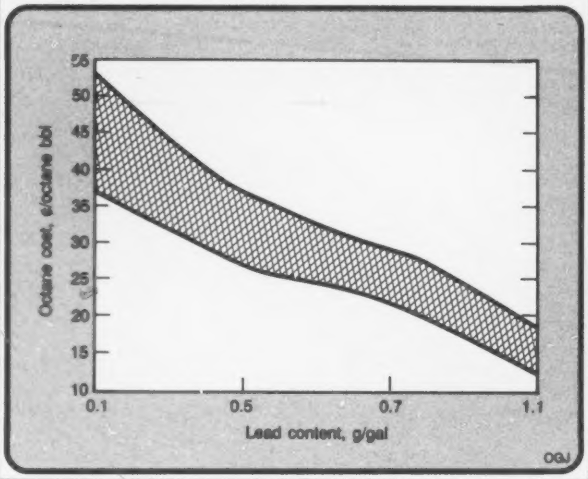
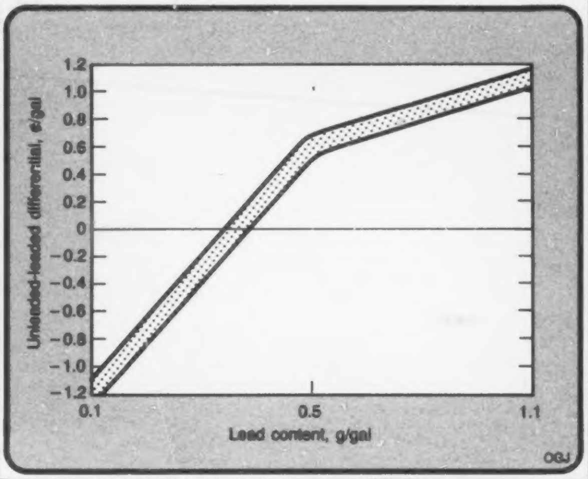


Fig. 5

Price of leaded regular will increase



natural gas, and nuclear energy for oil uses have further aggravated the situation. New export refineries in the Middle East and excess refining capacity, with excess octane-producing capacity in Europe, present stiff competition for U.S. refiners and marketers.

Increasing volumes of light refined products from foreign export refineries have appeared in the U.S. markets. Product imports of gasoline are given in Fig. 2. Imports have increased approximately 30% above 1984 levels. Although refined products demand increased by 3.4% in 1984 above 1983, reversing a trend of declining refined products consumption, the domestic refining industry has continued to contract.

Substantial excess domestic capacity, shortage of octane-producing capacity, and increased products imports have contributed to the pressures on the U.S. refining industry.

**Auto requirements.** Tetraethyl lead, the primary form of lead additive for octane improvement in gasoline, gives the greatest octane response to paraffinic naphtha. For example, the octane of LSR naphtha or natural gasoline (both highly paraffinic) is improved by 10 to 12 octane numbers with the addition of 1.1 g/gal lead.

Because of the lead phasedown rules, paraffinic stocks will become less desirable blend components in gasoline. Economics will force less LSR material to be blended into leaded gasoline (Fig. 3).

As mileage requirements increase, auto makers must continue to marginally increase compression ratio which in turn increases octane requirements to prevent excessive knock. This has resulted in decreasing customer satisfaction with domestic automobiles since 1974. The compression ratio has gradually increased in each of the past few years (Table 1). Although compression ratios are expected to increase past 9:1, thus heightening demand for octane, car makers will not exceed available octane supplies.

**LP model.** To properly analyze the impact of lead phasedown, Pace has developed a linear program (LP) model of the U.S. refining and petrochemical industry which represents the Petroleum Administration for Defense Districts (PADDs) 1 through 4. and uses the Pace Modeling System (PMS).

Such a complex model is required to prevent over-optimization of the industry. In the real world, companies compete for market shares, and intermediate product streams are not widely traded between companies. The model accounts for transportation costs of crude oil, products, and intermediates. It also accounts for aromatics production via reforming, toluene dealkylation, and olefins cracking.

The refining industry is represented by three types of refiners ranging from moderate to high complexity. Also included is a representation of the olefins industry and its interface with the refining industry. Based on the LP model, several implications for the refining industry are evaluated in light of lead phasedown.

**Clear pool octane.** All refiners will have higher marginal octane costs because of the removal of lead from the gasoline pool. The clear road octane of leaded gasoline will increase an average of about five octane numbers. As a result, leaded regular clear octane will be higher than unleaded regular (Table 2).

**Marginal octane costs.** Marginal costs of octane are shown in Fig. 4, which indicates that the industry average marginal cost increases dramatically as lead is removed from the gasoline pool. Low complexity refiners will be faced with a dramatic increase in octane costs, while high complexity plants will experience an increase of about $0.20/road octane barrel to over $0.40/bbl.

A refiner has limited control over the amount of straight-run naphtha in crude oil or the amount internally produced. However, natural gasoline purchases can be controlled. If such purchases cease, refiners in PADDs 1-4 would still have an estimated excess 100,000 b/d of light-straight-run naphtha over-optimized operation with LSR naphtha at fuel value.

**Gasoline pricing.** After banked lead rights have been used, leaded gasoline should no longer be the low-cost grade. At current octane levels, leaded gasoline at 0.1 g/gal requires a higher clear octane base stock than unleaded regular; so cost to the refiner will be higher than unleaded regular. The higher cost eventually should be reflected in consumer prices.

Under equilibrium conditions, the cost differential between unleaded and leaded regular as lead is reduced in the gasoline pool is given in Fig. 5. Leaded gasoline users should switch to cheaper unleaded grades if their cars are satisfied with the lower octane.

The independent testing company, Coordinating Research Council Inc. (CRC), has compiled data indicating a consumer satisfaction level of about 80% for the older leaded cars when using current unleaded regular gasoline. Others may be willing to accept poorer performance for lower price.

**LSR to olefin crackers.** Probably the most significant result of our recent analysis is the conclusion that a substantial portion of the octane shortage faced by the refining industry as a

Table 1

## Auto compression ratios continue to increase

| Model Year | Compression ratio |
|---|---|
| 1979 | 8.30:1 |
| 1980 | 8.40:1 |
| 1981 | 8.50:1 |
| 1982 | 8.58:1 |
| 1983 | 8.66:1 |

Source: CRC Octane Number Requirement Survey, Coordinating Research Council Inc., Atlanta, Ga.

Table 2

## Leaded clear octane higher than unleaded regular

| | Octane number (R+M)/2 | | | |
|---|---|---|---|---|
| | Specification | Clear at 1.1 g/gal | Clear, at 0.5 g/gal | Clear, at 0.1 g/gal |
| Unleaded regular | 87 | — | — | — |
| Leaded Regular | 89 | 83.6 | 86.3 | 88.2 |
| Unleaded premium | 91 | — | — | — |

R = Research
M = Motor octane

result of lead phasedown can be mitigated by routing low octane naphtha to feedstock for steam crackers.

The greatest benefit is derived when light straight run paraffinic naphtha and aromatics-extraction-unit raffinate are removed from gasoline blends. The most readily available and cost effective alternate disposition for this material is as olefins feedstock.

The highly integrated major refining companies with associated petrochemicals operations are already in a position to take advantage of this synergism. However, logistical constraints (lack of pipelines, terminals, etc.) will limit full use of this option for octane relief in the short term.

Much of the light naphtha has been derived from natural gasoline recovered by natural gas processing plants and routed to refiners as leaded gasoline blendstock. Many of these refiners do not have immediate outlets to petrochemicals operations and will not be able to accommodate the low octane material at the more restricted gasoline lead levels.

As traditional outlets for this material decline, natural gas processors will feel the pinch first. Not surprisingly, the major oil companies will be in the best position to absorb the distressed-price material and route it to integrated refinery/petrochemical operations.

**Sub-octane leaded.** A short-term mitigation step is the introduction of a sub-octane leaded gasoline in 1986. CRC consumer satisfaction data indicate that an 86 (R+M)/2 leaded grade of gasoline might capture about a 4% market share in 1986.

Suppliers who have historically relied on high volume sales of leaded gasoline, because of local market considerations and refinery octane limitations, might find this introduction of a lower octane grade of gasoline an effective way to maintain market share during the transition period. Preliminary analysis shows that in 1987, the sub-octane grade is expected to increase as a percentage of the total gasoline pool, first as a leaded fuel and then as an unleaded fuel, with the potential of becoming a third grade of unleaded gasoline.

**Use of lead credits.** Under EPA lead-reduction rules, lead rights or credits were allowed to be banked from Jan. 1, 1985, to Dec. 31, 1985, to help alleviate domestic shortages of octane. All lead credits must be used by Dec. 31, 1987. We are now in the period where lead credits may be used. EPA tabulations of lead banking for the first quarter of 1985 show that 3.4 billion g of lead were banked.[1] Approximately 0.1 billion g (or 2.9%) were based on imported blend stocks.

Approximately 217-million gal of leaded gasoline were consumed in the first quarter of 1985, which results in an average gasoline lead concentration of 0.73 g/gal.

It is expected that the second quarter bank will be slightly higher than the first quarter, with only small amounts banked in the third and fourth quarters. Therefore, we estimate that approximately 7.1 billion g of lead have been banked in 1985.

Knowing the amount of lead credits, projected leaded gasoline demand, and octane costs, the optimum use of lead credits can be determined. Octane costs are expected to be highest in 1986, and then decline in 1987. This would result in a lead concentration of 0.5 g/gal through the first quarter 1987.

The downside risk of holding lead credits is the declining leaded gasoline market. As the cost of leaded gasoline approaches unleaded gasoline, there is less incentive for fuel switching (leaded in autos designed for unleaded). However, the subgrade leaded regular will extend the time leaded gasoline will be available because a price incentive for the lower octane subgrade will exist.

**Imports.** Refined products imports are of primary concern to the refining and marketing industries in the U.S. Substantial changes have occurred both in the volume and source of refined products imported into the U.S. Gasoline imports have increased substantially for the past 3 years as shown in Fig. 2. Imports could present a real threat (especially if subsidized by exporting governments) to domestic markets.

Middle East gasoline plus distillate exports increased by 270% between 1983 and 1985. Europe will also export increasing volumes of gasoline to the U.S. during 1986 and 1987.

In particular, U.S. Gulf Coast refiners compete with Rotterdam for markets on the U.S. East Coast. The ability of the Gulf Coast refiner to compete effectively for this market is limited by the relative cost of transporting product to the East Coast, as well as current and possible future tariffs on imported products from Rotterdam.

The cost of transporting incremental products from the U.S. Gulf Coast to the East Coast via pipeline is close to the transportation cost for product from Rotterdam to the East Coast. The imposition of a tariff of 1.25 ¢/gal on gasoline and 0.25¢/gal for distillates provides some advantage for the Gulf Coast over Rotterdam in marketing on the U.S. East Coast. However, this tariff does not totally compensate for the feedstock advantage of the Rotterdam refinery. The current and projected higher lead usage in Europe compared to the U.S. will result in lower operating costs in Europe compared to the U.S. Gulf Coast. Incremental octane costs are lower in Europe than in the U.S. since incremental octane can often be obtained via leading in Rotterdam; in the U.S., octane must be obtained via processing.

If octane shortages cause gasoline prices to rise relative to crude prices, the European refining industry is equipped to increase exports of unleaded regular to New York. For example, if New York unleaded regular gasoline prices exceed Middle East crude by $0.11/gal, Europe could economically produce about 200,000 b/d unleaded regular gasoline for export to New York. Therefore, pressure on U.S. gasoline pricing due to domestic octane shortfalls will not produce significant gasoline price increases but will produce higher import volumes.

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Capital investment for octane should be evaluated carefully in light of declining octane demand in 1987 and the increased potential for gasoline imports from Europe. Noncapital alternatives such as the production of subgrade leaded gasoline and the optimal use of lead credits should be evaluated. They appear to be the most profitable for refiners.[1]

**Reference**

1. Personal conversation with James Caldwell, Environmental Protection Acency, Washington, D.C., Nov. 26, 1985.

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# Lead, vapor pressure reductions refining and gas processing

**L. Douglas Smith**
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Refiners have altered their operations to accommodate the requirements of the U.S. Environmental Protection Agency's (EPA) lead phasedown rules that went into full effect (maximum 0.1 g/gal) on Jan. 1 of this year. Anticipated new rules governing maximum gasoline vapor pressure will cause further adjustment.

Gas processors and gasoline marketers will also be affected.

In general, the moves made by refiners to increase octane capability have followed earlier projections.[1] We projected that about 250,000 b/d of $C_5/C_6$ isomerization would be built—almost 200,000 b/d has already been announced.

We estimated that about 500,000 b/d of reforming capacity would be modified or replaced—more than 100,000 b/d of new reformers and almost 200,000 b/d of reformer revamps have already been announced.[3]

The use of methyl tertiary butyl ether (MTBE) and alcohol is up dramatically, also as expected.

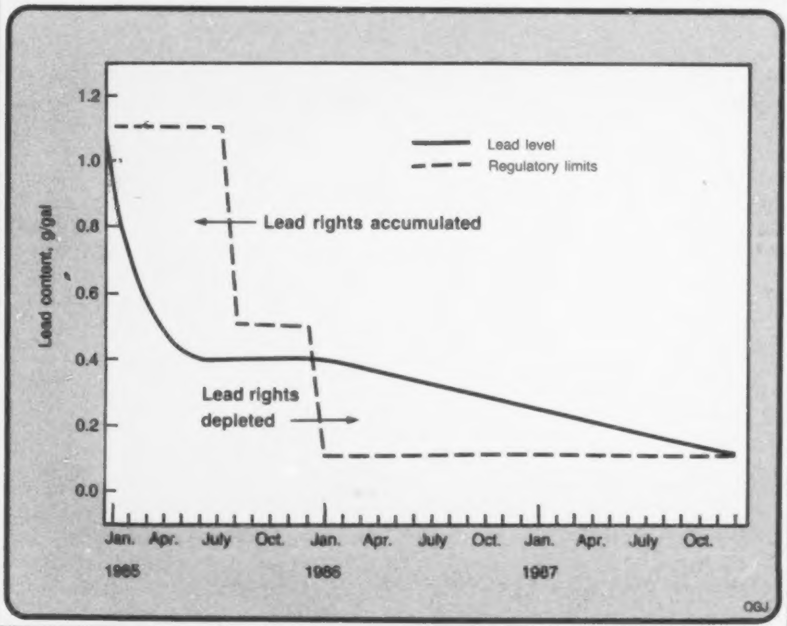
An important new development in octane improvement has been the use of "high octane" fluid catalytic cracking (FCC) catalysts. These catalysts have contributed a significant direct octane increase by raising FCC gasoline octane and an indirect effect by increasing FCC olefin production, allowing an increase in the production of high-octane alkylate.

Increasing alkylate production in the summer of 1985 dramatically increased refinery isobutane demand.

**Lead content and banking.** In the first half of 1985, the estimated lead level in regular gasoline was between 0.7 and 0.8 g/gal, well below the 1.1 g/gal limit, as refiners maximized ex-

Fig. 1

Expected trends in leaded gasoline lead content



# alter domestic operations

Table 1

## U.S. octane improvement*

| Announced projects | Capacity, 1,000 b/d | Typical (R+M)/2 increase | Million ON b/d |
|---|---|---|---|
| $C_5/C_6$ isomerization | 186 | 10 | 1.9 |
| New reformers | 105 | 4 | 0.3 |
| Reformer revamps | 176 | 4 | 0.6 |
| MTBE | 23 | 20 | 0.5 |
| Alkylation | 42 | 10 | 0.4 |
| FCC revamp | 188 | 1.5 | 0.2 |
| Subtotal announced projects | | | 3.9 |
| Additives | | | 1.2 |
| | | | 5.1 |

* 1988 vs. first half 1985.

Table 2

## Growth of U.S. gasoline pool octane requirements

| | 1983/84 | First half 1985 | Second half 1985 | 1988 |
|---|---|---|---|---|
| Volume, million b/d | 6.4 | 6.4 | 6.4 | 6.4 |
| Maximum regular gasoline lead level, g/gal | 1.1 | 1.1 | 0.5 | 0.1 |
| Estimated actual lead level, g/gal | 1.1 | 0.75 | 0.4 | 0.1 |
| Pool (R+M)/2 required (clear basis) | 86.3 | 87.0 | 87.3 | 87.8 |
| Octane number barrel increase, million ON bbl | | | | |
| Compared to 1983/84 | — | 4.5 | 6.4 | 9.6 |
| Compared to first half 1985 | — | — | 1.9 | 5.1 |

isting octane production in order to bank lead credits for use in 1986 and 1987. Using an approximation of about 40% of the U.S. gasoline pool as regular leaded, refiners banked more than 6 billion g of lead during the first half of 1985.

Refiners continued to bank lead in the second half of 1985. Regular gasoline lead level will probably be about 0.4 g/gal for the second half of 1985 vs. the maximum of 0.5 g/gal with refiners saving this additional lead for use in 1986 and 1987.

Fig. 1 shows the approximate lead level of regular leaded vs. the limits, showing the gradual drawdown through 1986 and 1987 of the lead "bank" built up in 1985. The effect of total lead savings in 1985 should allow a lead level between 0.2 and 0.3 g/gal for the years 1986 and 1987 vs. the maximum of 0.1 g/gal.

**Current pool octane.** Estimated pool octane in the first half of 1985 was up to 87.0 (research + motor)/2 (R+M)/2 clear vs. 86.3 in the 1983/84 time period. Since gasoline production was about constant at 6.4 million b/d this is in an increase of 4.5 million octane number barrels (ON bbl).

This increase was brought about by several changes. First, refiners increased severity in existing reformers up to the maximum. We estimate this accounted for as much as 2.5 million ON bbl, over half the requirement. This means that the severity was increased by 3 to 4 numbers on some 500,000 b/d of reforming capacity.

A second major change was the use of high octane FCC catalysts. Davison Chemical Division, W.R. Grace & Co., believes that an additional 1 to 1.5 million ON b/d are now being made in the U.S. using these high octane FCC catalysts.

Use of alcohols and other additives is up substantially. For example, ethanol usage is up to 49,500 b/d vs. 37,000 b/d in 1984, an increase of 38%. Further, isomerization units for upgrading the octane of $C_5/C_6$ paraffins have come on line in 1985, for example, at American Petrofina, Port Arthur, Tex., and Amoco, Whiting, Ind.

**Future pool octane.** The increases necessary to meet longer-term octane demand levels are going to come from the same areas: new continuous reformers, increases in existing reformer severity, octane catalysts, additives, and additional isomerization units. By 1988, with lead usage at a maximum of 0.1 g/gal in the regular leaded gasoline, and unleaded premium gaining a larger market share, we estimate pool octane requirements will be 87.8 (R+M)/2, an increase of 9.6 million ON bbl over the 1983/84 base and 5.1 million ON bbl over the first half of 1985.

Announced projects will account for about 3.9 million ON bbl as shown on Table 1. The majority of this increase will come from $C_5/C_6$ isomerization. Reported $C_5/C_6$ isomerization units to be put on line during 1986 and 1987 total 186,000 b/d. With an average 10 octane number increase this would be about 1.9 million ON bbl. Further use of additives (including MTBE) should add another 1.5 to 2 million ON bbl.

Some of the remaining requirement of 1 to 2 million ON bbl will come from additional changeouts to high-octane FCC catalysts, while reformer modifications and replacements will add almost 1 million ON bbl. Construction on many of these octane improvement projects is already underway.

Table 2 shows our forecast of the gasoline and octane pool situation and lead levels for 1983/84, first half 1985, second half 1985, and 1988. Pool octane requirements grow considerably through the period as lead is phased out.

**Domestic octane position.** Domestic refiners have committed a substantial amount of capital investment in order to produce the required octane levels due to the lead phasedown mandates dictated by EPA. We forecast that these conditions will be adequate to meet octane requirements, but octane will, in general, continue to be tight. Gasoline prices will rise (relative to crude) as refiners attempt to recoup investments and increased operating costs; however, the potential for low cost imported octane and domestic competition will moderate the market value of octane, allowing only a marginal return on these U.S. octane investments.

Although varying individual company situations make generalizations difficult, certain conclusions can be drawn from the reactions of refiners to the lead phasedown. Conversion of idle reformers to isomerization service appears to be the chosen path if an idle unit is available. Only large grass roots units, which would gain a cost of scale advantage, are being planned.

We believe either revamps or larger scale grass roots units will be marginally attractive if the cost to produce an octane barrel is below 40¢.

**Gas processors.** In addition to the effect on refiners, there is a substantial

Table 3

## Gasoline grade distribution and octane demand

| | % Leaded regular @ 89 (R+M)/2 | % Unleaded regular @ 87 (R+M)/2 | % Unleaded premium @ 91.5 (R+M)/2 | Clear pool octane (R+M)/2 |
|---|---|---|---|---|
| 1984 | 40 | 43 | 17 | 86.2 |
| 9 mo. 1985 | 36 | 46 | 18 | 86.7 |
| Estimated 1986 | 32 | 48 | 20 | 87.4 |
| Bonner & Moore* | 17 | 65 | 18 | 88.0 |
| Chevron† | 5 | 70 | 25 | 88.2 |
| Purvin & Gertz | 15 | 60 | 25 | 88.1 |

* Estimated refining cost impact of reduced gasoline vapor pressure, July 10, 1985, p. A-12.
† OGJ.

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**Smith**

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effect on gas processors. Domestic natural gas plant production of normal butane is about 210,000 b/d with almost 75% of this normal butane going to refineries. With increased reformer severities, substantial isomerization of $C_5/C_6$, and increasing use of alcohols, while gasoline production is relatively flat, refinery requirements for normal butane will be decreased.

Normal butane purchases by refineries in 1983/84 were about 150,000 b/d but we estimate they will be down to less than 120,000 b/d by 1988, with all of this decline due to the lead phasedown. Although this is a relatively small volume of butane to refiners, it is a very substantial portion of the butane produced by gas processors. This demand reduction should put downward pressure on butane price, as butane, which previously went to refineries, will be going into the fuel and petrochemical markets, competing with propane and ethane.

On the other hand, refinery demand for isobutane increased in 1985 as refiners produced additional alkylate. The 1985 average refinery demand for isobutane was about 150,000 b/d, up from 120,000 b/d in 1984.

This increased demand for isobutane and the reduced demand for normal butane resulted in a wider than normal spread in butane prices—6¢/gal in June 1985 vs. 3.5¢/gal in June 1984. The increased isobutane volumes have come from both increasing imports and increasing normal butane isomerization.

These higher demand levels for isobutane should continue as refiner demand for alkylation feed rises. This will lead to a wider spread in the normal/isobutane price.

**Retail marketing.** Wholesale and retail marketing are beginning to show the effects of lead phasedown. Early in January 1986, the leaded/unleaded spread on the Gulf Coast spot market was only 1¢/gal. Prices at the pump in the Houston area then began to show the effect of this change. The 4¢ to 6¢ historic differential closed to zero at some stations, while a 1-2¢/gal spread was typical.

Premium unleaded demand continues to increase and is being pushed heavily in a number of major company advertising campaigns. We expect premium unleaded demand to continue to grow through the remainder of this decade, reaching about 25% of the total gasoline volume by 1990.

Table 3 shows the historic and forecast gasoline splits and the resulting pool octane requirements. These data show the dramatic increase in gasoline octane for 1985 vs. 1984 and the even more dramatic increase from 1985 to 1986.

Lead phasedown and lead banking are also the likely cause of unusual disparities in region to region gasoline pricing. For example, the Group 3 leaded/unleaded differential is wider than on the Gulf Coast. With a higher percentage of leaded gasoline produced in 1985, the Group 3 refiners banked more lead and, thus, are now able to produce a higher lead level (and lower cost) regular than Gulf Coast refiners.

**Volatility reduction.** A further substantial change in butane demand is likely as the EPA looks to reduce vapor emissions from automobiles. A recent EPA study indicates that emissions are far above expectations.

A number of possible scenarios has been proposed to lower the vapor pressure of gasoline. These would include using either the Evaporative Index (EI) or the Front End Volatility Index (FEVI) as a specification for gasoline volatility.

Both of these equations use vapor pressure and front-end distillation. Our calculations indicate that using the EI specification as defined in the DuPont waiver would reduce gasoline vapor pressure by about one psi.

EPA will likely reduce the effective vapor pressure of gasoline by introducing new vapor pressure or volatility limits. Vapor pressure will likely be lowered by at least 1 psi. Such legislation would reduce refinery normal butane demand (year average) by over 100,000 b/d.

Using typical price differentials between normal butane and unleaded gasoline, this would cost a 100,000 b/d refinery over $5 million/year in lost earnings. Since this legislation would likely effect all refiners more or less equally, these reduced earnings may be offset by increases in light product prices.

The effect on gas processors would be substantial. Gas processors will lose about 15% of their butane market due to lead phasedown. A reduction in gasoline volatility specifications by 1 psi Rvp would virtually eliminate normal butane purchases by refiners. This would have a substantial further downward effect on the pricing of butane.

A downward movement of propane and ethane would also likely ensue as the excess butane would be competing with them in the petrochemical feedstock and fuel markets. This downward movement of ethane-propane-butane should make these feeds more attractive for ethylene cracking, reducing liquid cracking demand.

Adoption of more strict volatility limits will change refiner economics among the various octane-upgrading possibilities. Upgrading schemes such as $C_5/C_6$ isomerization and alcohol blending, both of which increase vapor pressure, will be less attractive relative to reforming, for example, should volatility restrictions be tightened.

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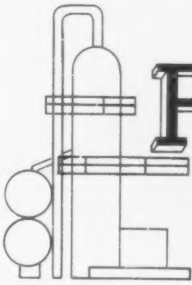
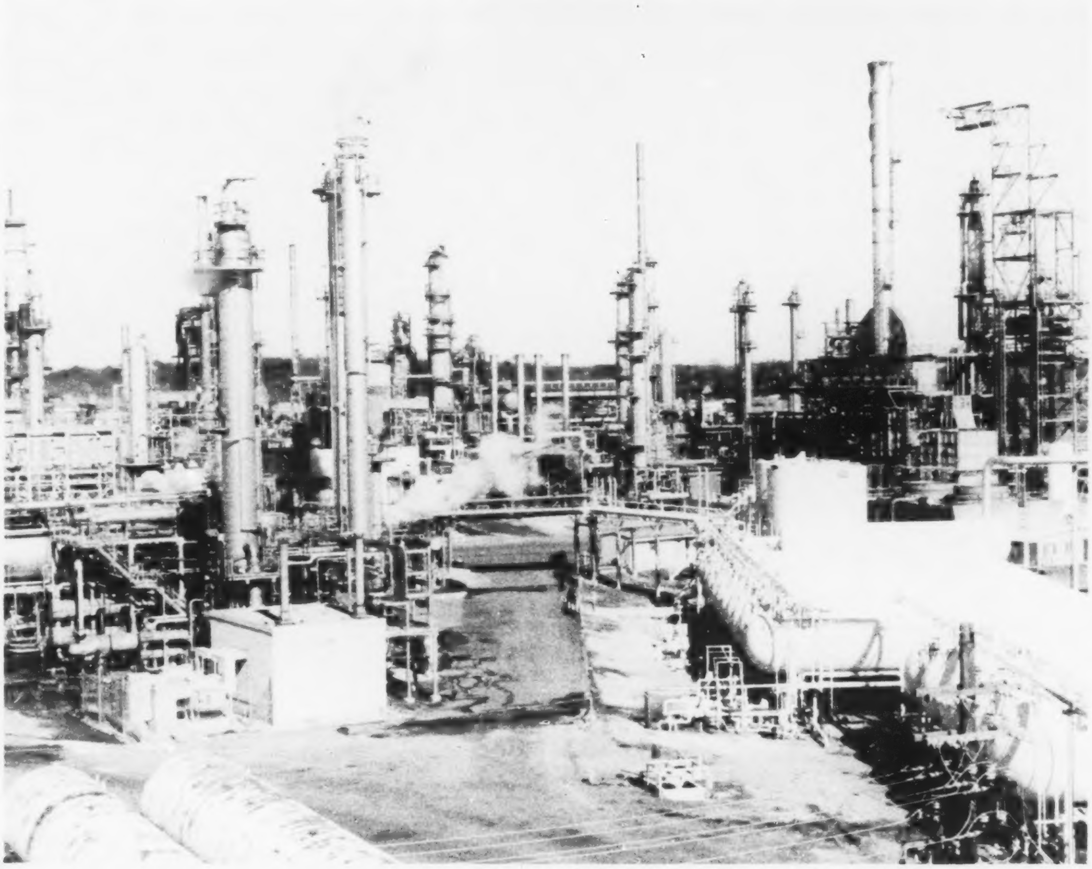
1. Smith, L. Douglas, "Lead phasedown problems not restricted to refiners," OGJ, June 24, 1985, p. 95.
2. Obel, Michael, "U.S. refiners poised for move into next lead phasedown step," OGJ, Dec. 23, 1985, p. 15.

## OGJ REPORT



# REFINING REPORT



**U.S. refiners** have been meeting the tough requirements of EPA's tougher lead phasedown rules by modifying some process operations, revamping others, and making use of the latest catalyst developments.

# Industry restructures, capacity up slightly

**Richard A. Corbett**
Refining Editor

The U.S. refining industry may be starting to see a better economic picture, according to the Journal's latest survey of U.S. refineries. Crude oil charged to refineries was up slightly in 1985, and refinery utilization has improved.

The industry has restructured somewhat with three major refineries changing hands and a new refinery started in Alaska.

The industry also continues to strenghten its downstream processing technology. Almost all of the downstream processes scored capacity gains.

Table 1

## Crude capacity up slightly, isomerization projects jump

| | Capacity 1,000 b/d | | | | Construction 1,000 b/d | | |
|---|---|---|---|---|---|---|---|
| | As of 1-1-86 | As of 1-1-85 | % change from 1-1-85 | Vol change from 1-1-85 | 1986 completions* | Est. % change by 1-1-87 | 1987 completions* |
| Crude, b/cd | 15,258.2 | 15,136.2 | +0.8 | +122.0 | 23.5 | +0.1 | 70.0 |
| Feed, b/sd | | | | | | | |
| Thermal operations | 1,847.8 | 1,810.1 | +2.1 | +37.7 | 30.5 | +1.7 | — |
| Cat reforming | 3,673.0 | 3,671.3 | — | +1.7 | 10.0 | +0.3 | 33.5 |
| Cat cracking (fresh feed) | 5,234.1 | 5,165.9 | +1.3 | +68.2 | 60.0 | +1.1 | |
| Cat hydrocracking | 1,139.3 | 1,063.0 | +7.2 | +76.3 | — | — | — |
| Hydrorefining | 2,191.5 | 2,324.6 | −6.1 | −133.1 | 12.0 | +0.5 | — |
| Hydrotreating | 6,592.8 | 6,525.1 | +1.0 | +67.7 | 73.8 | +1.1 | — |
| Products, b/sd | | | | | | | |
| Alkylation | 940.3 | 912.8 | +3.0 | +27.5 | 15.0 | +1.6 | — |
| Aromatics and isomerization | 581.7 | 460.4 | +26.4 | +121.3 | 100.0 | +17.2 | 16.0 |
| Lubes | 235.4 | 232.3 | +1.3 | +3.1 | 6.0 | +2.5 | |
| Coke, 1,000 ton/day | 70.0 | 68.1 | +2.8 | +1.9 | — | — | — |
| Asphalt | 692.0 | 678.6 | +2.0 | +13.4 | — | — | — |

* Based on reported projects known to date.

Crude-charging capacity increased 0.8% to 15,258,214 b/cd from 15,136,262 b/cd as of Jan. 1, 1986 (Table 1). All of the downstream processes except hydrorefining saw capacity gains exceeding 1%. Hydrorefining shows a significant drop in part because Chevron U.S.A. did not report 60,000 b/d from the Perth Amboy, N.J., refinery, and Atlantic Refining & Marketing did not report 74,000 b/d from the Philadelphia refinery.

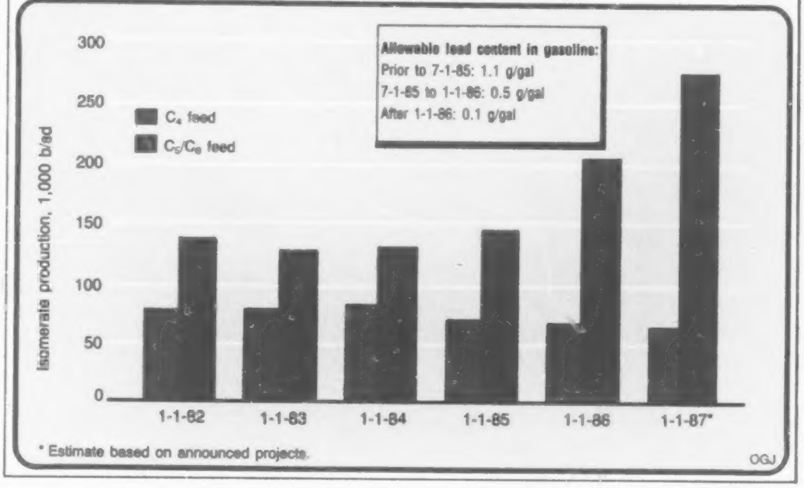
$C_5/C_6$ isomerization capacity scored a dramatic jump in response to the Environmental Protection Agency's lead phasedown rules that went into full effect on Jan. 1. More than 55,000 b/sd of new isomerization capacity went onstream—a gain of more than 26%, to about 200,000 b/sd (Fig. 1). Announced start ups in 1986 will add about 70,000 b/sd more.

$C_5/C_6$ isomerization helps refiners increase the octane number of the $C_5+$ portion of light-straight-run naphtha and natural gas liquids. This portion was previously upgraded by adding lead antiknock compounds.

The process—in many cases a revamp of an idle catalytic reformer—requires a relatively small investment. It is estimated that a 5,000 b/d $C_5/C_6$ once-through isomerization unit, based on a reformer revamp, will cost about $2.6 million including catalyst.

Fig. 1

## Lead phasedown spurs $C_5/C_6$ isom projects



* Estimate based on announced projects.

Refinery utilization, input to crude distillation units divided by operable crude capacity, began improving in March 1985 and, despite a drop between July and September, has remained higher than previous years (Fig. 2). This indicates refiners have tightened their operations and improved operating efficiency.

Catalytic hydrocracking gained capacity (up 7.2%, Table 1) indicating improved heavy oil processing capability. A large part of this was a 50,000 b/d addition at Shell Oil Co.'s Deer Park, Tex., refinery. This should help Shell take advantage of the light-crude/heavy-crude cost margins expected to improve by 1990.

The big concern for refiners in 1985 was the EPA's lead phasedown rules. Other articles in this special report address the effects of lead phasedown and how one refiner is meeting the requirements.

**Major and minors.** Considerable restructuring occurred among refiners with more than 200,000 b/cd crude capacity. They saw a reduction in crude charging capacity to 11.506

Table 2

## Reformer and FCC feed pretreat show gains

| | Capacity 1-1-86 1,000 b/sd | Capacity 1-1-85 1,000 b/sd | % change |
|---|---|---|---|
| **Hydrorefining** | | | |
| Resid and heavy gas oil | 720.5 | 856.1 | −15.8 |
| FCC and cycle stock pretreatment | 1,015.0 | 913.0 | +11.1 |
| Mid distillate | 435.0 | 534.5 | −18.6 |
| Other | 21.0 | 21.0 | 0.0 |
| **Hydrotreating** | | | |
| Cat reformer feed and naphtha desulfurization | 4,007.6 | 3,728.3 | +7.5 |
| Straight run distillate | 1,135.4 | 1,086.3 | +4.5 |
| Other distillates and material | 1,331.8 | 1,337.5 | −0.5 |
| Lube oil polishing | 186.6 | 165.9 | +12.5 |
| Naphtha olefin and aromatics saturation | 201.1 | 210.1 | −4.3 |

Table 3

## Major companies (200,000+ b/d crude capacity) restructure

| Company and rank | No. refineries | Crude, b/cd | Crude, b/sd | Cat. cracking (fresh feed), b/sd | Cat. reforming, b/sd | Hydro-cracking, b/sd | Hydrorefining-hydrotreating,* b/sd | Alkylation, b/sd | Coking, b/sd |
|---|---|---|---|---|---|---|---|---|---|
| 1. Chevron U.S.A. Inc. | 14 | 2,007,200 | 2,447.366† | 454,300 | 382,600 | 218,500 | 665,600 | 90,600 | 158,500 |
| 2. Exxon Co. U.S.A. | 5 | 1,200,000 | 1,267,000 | 508,000 | 281,000 | 759,000 | 667,600 | 89,500 | 111,000 |
| 3. Shell Oil Co. | 7 | 1,035,600 | 1,078,500 | 396,500 | 260,000 | 153,200 | 506,300 | 85,000 | 95,000 |
| 4. Amoco Oil Co. | 7 | 967,000 | 1,000,500 | 419,000 | 236,750 | 113,000 | 229,800 | 54,700 | 74,500 |
| 5. Texaco Refining & Mktg. | 8 | 903,000 | 970,400 | 332,000 | 224,300 | 89,000 | 317,500 | 52,000 | 121,000 |
| 6. Mobil Oil Corp. | 5 | 750,000 | 798,000 | 322,500 | 220,300 | 53,700 | 296,650 | 61,200 | 134,000 |
| 7. Atlantic Richfield Co. | 5 | 679,000 | 706,000 | 150,000 | 163,000 | 72,000 | 192,600 | 16,200 | 141,000 |
| 8. Sohio/BP | 4 | 655,100 | 685,000 | 229,700 | 177,700 | 80,000 | 135,000 | 47,900 | 47,400 |
| 9. Marathon Petroleum Co. | 4 | 588,000 | 611,000 | 178,000 | 152,400 | 22,000 | 112,000 | 42,600 | 24,000 |
| 10. Unocal Corp. | 4 | 497,000 | 519,400 | 144,000 | 142,000 | 54,500 | 104,600 | 30,200 | 78,900 |
| 11. Conoco Inc. | 5 | 390,000 | 404,500 | 106,100 | 80,400 | — | 175,500 | 20,500 | 69,300 |
| 12. Sun Co. Inc. | 3 | 358,000 | 379,000 | 165,000 | 103,600 | 28,000 | 43,900 | 27,400 | 7,300 |
| 13. Ashland Petroleum Co. | 3 | 346,543 | 357,220 | 148,000 | 85,500 | — | 165,200 | 24,900 | 55,000 |
| 14. Citgo Petroleum Co. | 1 | 320,000 | 330,000 | 150,000 | 91,000 | 35,000 | 54,000 | 23,000 | 63,000 |
| 15. Phillips Petroleum Co. | 3 | 300,000 | 326,000 | 155,400 | 68,000 | — | 216,600 | 26,600 | — |
| 16. Koch Refining Co. | 2 | 280,000 | 290,000 | 95,000 | 53,000 | — | 131,500 | 16,900 | 60,000 |
| 17. Champlin Petroleum Co. | 2 | 230,000 | 237,500 | 101,000 | 63,000 | — | 128,000 | 27,600 | 49,000 |
| **Total** | **82** | **11,506,443** | **12,407,386** | **4,054,500** | **2,784,550** | **994,800** | **4,142,350** | **736,800** | **1,288,900** |

* Excludes pretreating catalytic reformer feed, naphtha desulfurization, and napntha, olefin, or aromatics saturation.
† Calculated from either stream day or calender day figures.

million b/cd in 1985 from 11.882 million b/cd the previous year (Table 3). And the group's refineries now total 82 compared with 89 last year.

Much of the restructuring came from mergers and aquisitions. Texaco closed two refineries; Lawrenceville, Ill., and Amarillo, Tex., and sold the Westville, N.J., refinery to Coastal Eagle Point Oil Co. It also combined the reported capacities of its Port Arthur and Port Neches refinieries.

Chevron U.S.A. Inc., after aquiring Gulf Oil Products Co.'s refineries, sold its Belle Chasse, La., refinery to Sohio/BP and closed its Baltimore, Md., refinery. Atlantic Richfield Co. sold its Philadelphia refinery to Atlantic Refining & Marketing Corp. And ARCO has started a 12,000 b/cd refinery in Kuparuk, Alas.

Despite the restructuring, this industry segment still acounts for 75.4% of the U.S. refining capacity. It continues to be flexible, and utilizes some of the most advanced downstream technology in the industry.

The segment made up of companies with less than 200,000 b/cd capacity has boosted its share of U.S. refining capacity (Table 4). Its share is now 24.6 % of the U.S. capacity.

Some of this is the result of purchases from major refining companies. But other increases are the result of restarting shut down facilities.

This industry segment also showed gains in downstream capability, with notable increases in catalytic cracking and hydroprocessing.

Through restructuring and upgrades, the U.S refining industry appears to be successfully meeting the effects of tough market circumstances and government rulings. If 1985 results continue, the industry will be well prepared for the 1990s. •

Table 4

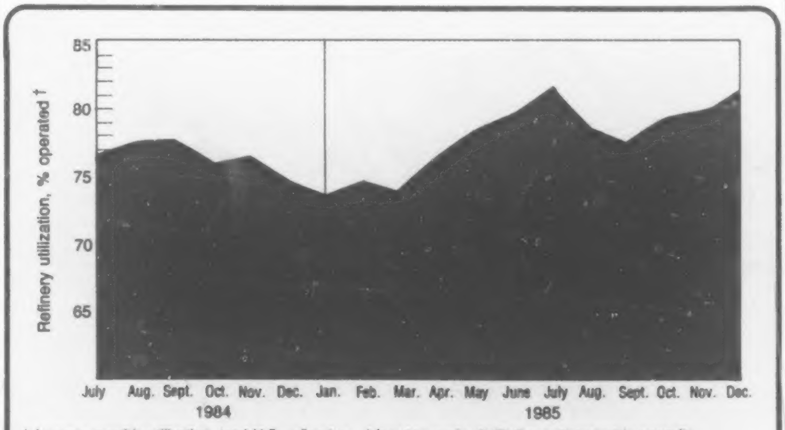
## Smaller refiners gain capacity share*

| | Companies with 200,000+ b/cd crude capacity 1-1-86 | Companies with 200,000+ b/cd crude capacity 1-1-85 | Companies with less than 200,000 b/cd crude capacity 1-1-86 | Companies with less than 200,000 b/cd crude capacity 1-1-85 |
|---|---|---|---|---|
| No. companies | 17 | 18 | 82 | 81 |
| No. refineries | 82 | 88 | 107 | 103 |
| Capacity, b/cd | 11,506.4 | 11,833.2 | 3,751.8 | 3,253.0 |
| Capacity b/sd | 12,069.4 | 12,397.6 | 3,934.5 | 3,500.6 |
| % U.S. capacity (b/cd basis) | 754 | 78.2 | 24.6 | 21.5 |
| Cat. cracking (F.F.), b/sd | 4,054.5 | 4,168.0 | 1,179.6 | 997.9 |
| % on crude | 33.5 | 33.6 | 30.0 | 28.5 |
| Cat. reforming, b/sd | 2,784.6 | 2,941.4 | 888.4 | 730.0 |
| % on crude | 23.1 | 23.7 | 22.6 | 20.8 |
| Hydrocracking, b/sd | 994.8 | 955.3 | 144.5 | 107.7 |
| % on crude | 8.2 | 7.7 | 3.7 | 3.1 |
| Hydrorefining and hydrotreating, b/sd† | 4,142.4 | 4,341.9 | 702.9 | 450.8 |
| % on crude | 34.3 | 35.0 | 17.9 | 12.9 |
| Alkylation, b/sd | 736.8 | 716.6 | 198.9 | 191.8 |
| % on crude | 6.1 | 5.8 | 5.1 | 5.8 |
| Coking, b/sd | 1,094.4 | 1,232.7 | 207.6 | 169.7 |
| % on crude | 9.1 | 9.9 | 5.3 | 4.8 |

* All companies 1,000 b/d
† Excludes pretreating cat. reformer feed, naphtha desulfurization, and naphtha olefin or aromatics saturation.

Fig. 2

## Refinery utilization improves



* Average monthly utilization, total U.S. refineries. † Input to crude distillation units/operable capacity.
Source: American Petroleum Institute.

OGJ

# Keller: Low oil cost won't save refiners

*Chevron chairman tells NPRA meeting crude price slide carries risks for complex plants, Cinderella role for fuel oil. Worsening resid conversion economics, gasoline volatility dispute, catalyst preservation and octane improvements also detailed.*

Plunging crude prices don't necessarily mean salvation for U.S. refiners, George M. Keller, Chevron Corp. chairman, told the National Petroleum Refiners Association annual meeting last month in Los Angeles.

Simple refineries with a strong focus on producing fuel oil will benefit as oil prices settle at very low levels. But as the spread between light and heavy oil prices narrows further, the economics of plants with a big investment in resid upgrading will deteriorate.

The worsening resid conversion return was detailed in an NPRA paper by John R. Dosher, managing partner of Pace Consultants Inc., Houston.

Keller warned NPRA members that netback crude pricing is not as attractive economically as some think and instead adds to refiners' long term woes.

Other threats to the industry can come with an oil import fee and tax reform proposals, he said.

Tougher rules on gasoline volatility and emissions controls, preserving catalysts, and boosting gasoline octane were among technical subjects on the program.

**Crude prices.** Keller acknowledged that lower crude prices are generally improving margins for small refiners but not for all refining segments.

Falling gasoline prices due to continuing intense market competition will keep some refiners from enjoying the higher margins from lower crude prices.

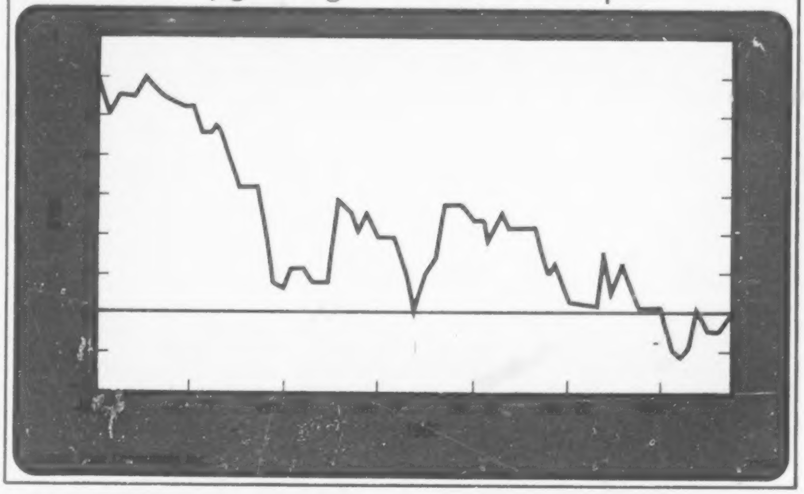
"On the other hand, if crude prices stabilized at extremely low levels, we could see a Cinderella role for fuel oil.

"At very low price levels, it would back out some natural gas and coal for industrial users with the flexibility to switch."

Thus older and less efficient refineries, especially ones that make a lot of fuel oil, would do pretty well in an era of very low crude prices.

But plants whose economics are based on the differentials between light and heavy crudes and light and heavy products will suffer as sagging crude prices shrink those differentials.

How resid upgrading economics slumped



"Certain new investments may look more attractive in this climate. In a cogeneration project, for example, your rate of return is based on the spread between fuel costs and power costs.

"But in general, it's very hard to see a whole lot of new big ticket capital investment downstream, even in projects that might improve efficiency, simply because lower prices are squeezing capital budgets that much further."

**Upgrading economics stung.** Very low crude prices will provide little incentive for investment in or operation of heavy oil conversion processes such as cat cracking, visbreaking, and coking, Pace's Dosher said.

Pace earlier conducted a study of the economic incentive of those processes based on crude oil at $25/bbl (OGJ, Oct. 28, 1985, p. 51). And with crude prices dropping, it estimated how the upgrading outlook might change with crude oil priced at $12/bbl and at $18/bbl.

Pace gauges the economic incentive to convert heavy oil by the heavy oil discount (HOD), which is the price difference between high sulfur residual fuel oil and 34° gravity crude oil.

The expected quick substitution of residual fuel for coal and natural gas undercuts the economics of heavy oil conversion, Dosher said.

With the current export price for U.S. steam coal at about $41/ton, competing residual fuel oil based on crude priced at $12/bbl would be more economic for many existing U.S. manufacturers.

And fuel oil based on a $12/bbl oil price competing with gas in East Coast utilities spurs a drop in the wellhead price of U.S. natural gas to $1-1.50/Mcf.

So crude oil at $12/bbl at first will displace natural gas under boilers in the U.S. and overseas markets, which already is happening.

But at $18/bbl little if any substitution occurs.

The pressure to substitute with fuel oil is further supported by recent swings in the HOD, which has dropped below zero (see chart). Thus, with high sulfur residual fuel oil selling at a premium to crude oil, there is currently no incentive to run bottoms-processing units such as cokers.

This disincentive for bottoms conversion has occurred early in industry's period of adjustment to lower crude oil prices and could change as the adjustment proceeds, Dosher said.

**Supply, demand.** Don't expect burgeoning crude demand to improve the HOD outlook soon, Pace contends, figuring how much world oil demand will increase with each 10% drop in crude prices. It estimates that oil demand will jump 0.35% in 1986, 0.75% in 1987, and 1.5% in 1988 and thereafter.

"Based on past experience, we expect a great deal of skepticism concerning this modest response of demand to price for petroleum. However, these values are consistent with the drop in demand that occurred as a result of the price increases during the 1970s, and we strongly believe the process is reversible to a large degree," Dosher said.

On the supply side, Pace thinks that depressed oil prices will cut oil production outside the Organization of Petroleum Exporting Countries and Mexico by 1% in 1986, and by as much as 10% in 1990, compared to output levels at $25/bbl.

At $12/bbl for crude, lost U.S. production from Offshore California, and stripper wells and enhanced oil recovery projects in Petroleum Allocation Defense districts I-IV would total 200,000 b/d in 1986, 408,000 b/d in 1987, 763,000 b/d in 1988, 800,000 b/d in 1989, and 835,000 b/d in 1990. At $18/bbl, PADDs I-IV stripper/EOR lost output would total 70,000 b/d in 1986, 175,000 b/d in 1987, and 250,000 b/d during 1988-90.

**Netback threat.** Keller blamed netback pricing arrangements for contributing to the rapid fall in crude prices and restructuring refiners' market roles.

"The biggest problem with netbacks is that they remove the manufacturers from their traditional place in the supply/demand connection, putting both ends of the string in the hands of the producers," he said.

Rather than stabilizing the market, netback arrangements have played a big part in the market's volatility.

"In a netback arrangement, the refiner is in a position similar to someone who receives a fee for performing a service rather than that of the traditional entrepreneur who has to gauge the risks of the marketplace. The risk is largely transferred to the supplier—the producer of the crude—whose primary interest is not meeting demand so much as getting rid of his commodity.

"This encourages a higher level of refinery utilization than the market requires.

"To that extent, it prolongs the agony of refining overcapacity."

**Taxes, import fees.** Keller thinks that eliminating investment tax credits, lengthening depreciation schedules, and allocating interest expenses on a consolidated basis would "have the effect of blighting the prospect of growth and renewal for Ameria's heavy industries."

He also is skeptical about the benefits of imposing fees on imported crude and products.

"I wonder just how much benefit would actually flow to those who are now being hurt by low-priced imports. I wonder how long it would be before the original intention got buried under a whole host of exemptions and exceptions and riders and amendments, until the fleas outweigh the dog."

Keller also sees inconsistency in industry voicing support for an oil import fee while opposing other new taxes. On the other hand, he called on the U.S. government to use its powers under the General Agreement on Tariff and Trade to stave off dumping of subsidized imported petroleum products.

**Gasoline volatility.** The Environmental Protection Agency's proposed new limits on gasoline volatility to limit air emissions has refiners and marketers at odds with automakers over who should accept the burden of controlling those emissions.

"There is little question that reducing gasoline volatility would reduce vapor emissions more rapidly than any other approach," Keller said. "And Stage II refueling controls (controls on retail gasoline pumps) could also make an impact faster than the alternatives."

"But the gain in timeliness is more than offset by the higher cost of these solutions. Looking at the long term, improved canisters offer far greater benefits than the other types of controls."

Still, there is room for compromise, he added.

General Motors Corp. thinks volatility controls should be applied on a regional basis only.

"We are advocating that controls be applied only in those areas of the country where ozone levels present an air quality problem, and only during the summer smog season," said Howard H. Kehrl, GM vice-chairman.

That approach would let the petroleum industry and the free market determine the most cost-effective means of regionalizing volatility control and limit controls to only about 10% of annual gasoline sales, he said.

Gasoline volatility control would immediately reduce emissions for the entire vehicle population vs. gradually improving emissions levels as would improved canisters and retail gasoline pump controls, said W.D. France, GM research lab assistant department head.

"An added advantage of reduced summer Rvp would be to decrease incidences of hot driveability problems in the summer which still occur for some vehicle owners," he said.

**Catalyst preservation.** The effectiveness of chemical passivation of vanadium in fluid cat cracking operations was shown in case studies presented by R.C. Barlow, assistant product manager of Betz Process Chemicals Inc., The Woodlands, Tex.

"Based on current theories, the passivation process is such that the mobile form of vanadium found in the FCC unit cracking system ($V_2O_5$) is essentially complexed chemically to form a nonmobile molecule," says Barlow.

"Thus catalyst poisoning is prevented."

Results of the commercial studies on vanadium passivation show that:

- It effectively reduces the detrimental effects of vanadium on an FCC catalyst.
- The microactivity loss due to vanadium can be reduced by 30-50%.
- The hydrogen and coke production due to the catalytic dehydrogenation effect of active vanadium can be cut by about 65%.
- Commercial passivation data doesn't appear to support a synergism between the vanadium and nickel passivation processes.

**Octane boons.** Several commercially proven, cost effective alternative processes to boost gasoline pool octane were unveiled by Deutsche BP and EC Erdolchemie, West Germany, and BP Ventures, London.

Key to the processes is the production of high octane methyl ethers from the reaction of olefinic feedstocks and methanol.

The processes include:

- The EC Erdolchemie MTBE process, which produces methyl tertiary butyl ether from isobutylene and methanol using a special process to separate methanol from the $C_4$ hydrocarbon raffinate.

Other benefits stem from using a bifunctional catalyst and hydrogen atmosphere that hydrogenates butadiene, thus lowering operating costs of a downstream alkylation unit.

- The EC Erdolchemie gasoline process, which reacts isoamylenes in catalytically or steam cracked naphtha $C_5$ cuts with methanol to give high octane tertiary amyl methyl ether.
- The BP cracked naphtha etherification process, which combines the reactive olefins in a cracked naphtha feed—ranging from $C_4$ through light cracked naphtha to full range cracked naphtha—with methanol to produce an upgraded naphtha containing a mixture of high octane tertiary alkyl methyl ethers. ▪

**Storage** at Tenneco Oil Co.'s 137,000 b/cd Chalmette, La., refinery holds heavy, high sulfur crudes and products made from those crudes. Refiners have been changing their strategies for managing stocks in line with market shifts.

# Refiners meeting U.S. demand with less product in inventory

**Michael Obel,** Staff Writer

Refiners in the U.S. are getting along with less product stocks than anyone dreamed possible in 1980, when inventories peaked.

Although demand started its long slide in 1979 in the U.S. and in 1980 in the non-Communist world, stocks continued to build. But the combination of high carrying costs, weakening prices, and declining demand sent stocks into a slide that has yet to stop.

Industry evolved a strategy of cutting product inventories as much as possible and holding just enough crude to meet specific demand hikes.

Along the way, low stocks emerged as a major force in firming spot prices.

The most recent lesson came with this season's heating oil market. U.S. refiners entered the current heating season with record low stocks. Industry held only 37 days' requirements, scarcely half the 1980 peak (OGJ, Dec. 2, 1985, p. 27).

Prices reached their highest level since February 1984, and there was no hint of shortage.

On the contrary, when weather turned cold in December the system sprang into action. January's mild temperatures, increased crude production and imports, and higher refinery runs resulted in a glut.

Many refiners, therefore, are more convinced than ever that they have yet to reach the lower limit of product inventories.

The crude and product drawdown that began

## Companies see stock trades as way to improve earnings

Some companies will not pull stocks down any more and risk interruptions to refineries or customers, but they will trade stocks to improve profit and loss statements.

Trading among refiners and marketers is not new, but it is a highly active part of the business and one of the few ways to earn money on inventories.

One of the main forms of trading is the opportunity trade, a move that can lower crude oil acquisition costs.

"We buy West Texas intermediate," said one official with Mobil Oil Corp. "On numerous occasions when we're not running it or trading it for another crude, you actually sell it. Then you turn around and buy Canadian crude cheaper. Even figuring in the yield loss on those deals, you can make as much as $3/bbl."

Mobil said it earned nearly $13 million last year on opportunity trades.

Lucrative as opportunity trades are, Mobil earned more with location trades, a move that can lower transportation costs.

Such exchanges "involve a crude that is produced in a strange place. If we have to deliver it to one of our refineries, it will cost quite a bit. So we shop around for a source closer to our refinery," the official said.

Last year location trades were worth more than $30 million to Mobil.

Another exchange is a quality trade. Most quality trades are sweet-for-sour deals, where a refiner with little upgrading capacity trades high sulfur crude for low sulfur crude owned by a refiner with substantial upgrading capacity. The exchange allows both refiners to enjoy lower unit operating costs.

Another exchange, called time trading, allows refiners to meet obligations during shutdowns and turnarounds.

"If one of our refineries has an operating problem, we'll immediately go into the market and try to time-trade the crude. You deliver the crude to someone else in exchange for some later," said the Mobil official.

"In the recent market, people have actually paid you more for close-in crude. That is, they give you the crude, plus money. So not only do you make money on the deal, you collect it a month early and get 1 month's worth of the time value of that money."

One company estimates that the 4.8 million bbl of crude it time-traded last year earned it a differential of 69¢/bbl.

Said a spokesman: "That's not very important, but it's what we do for a living. It's the icing on the cake. If you don't do it, you're not competitive."

nearly 6 years ago results from industry's decision to hold less products and more crude, relative to demand.

Such a strategy allows individual refiners to meet incremental demand increases with higher crude runs, rather than from product storage.

"The goal is to maximize inventory turnover and minimize tankage and inventory," says a Sun Marketing & Refining Co. official.

Changes in crude and product levels since their 1980 peaks show how refiners have implemented the strategy.

During their September 1980 peak, total product inventories were 977.835 million bbl. In December 1985 total product inventories were 696.7 million bbl, a 29% decline.

That contrasts with a much smaller change in crude oil inventories.

In September 1980 total crude oil inventories were 376.388 million bbl. In December 1985 total crude oil inventories were 321.9 million bbl, a 14.5% decline.

That the U.S. refining industry has increased crude inventories relative to demand can be seen by comparing recent crude stock levels with levels during a period of similar demand.

Crude stocks at yearend 1971 and yearend 1972 averaged 253.022 million bbl. Demand in 1971 and 1972 averaged 15.79 million b/d.

Crude stocks at yearend 1984 and yearend 1985 averaged 333.638 million bbl. Demand in 1984 and 1985 averaged 15.675 million b/d.

Despite nearly identical demand in 1971-72 and 1984-85, crude stocks rose 32%.

**New incentive.** Refiners started the stock drawdown early in the decade in response to high interest rates and slowly weakening prices.

Today a new incentive, the growing volume of crude and product traded on the spot market, drives refiners to look for more ways to reduce product inventories.

"The big thing in the past has been that the spot market has been smaller than the posted market," says John A. Matson, managing director of Pace Consultants Inc., Houston.

"In the last 18 months the spot market became dominant. As a result, spot prices for product have been leading spot prices for crude in many instances, so your vulnerability on inventory has been greater.

"Say on any given day the spot price of product and the spot price of crude are well related. All of a sudden the spot crude price moves down.

"What happens is the spot product price will leap further down. With spot volumes greater than they have been, the lost value increases since there is very little support from the posted price market."

**Disincentives.** Not all refiners face the same economic pressure to cut inventories.

Refiners that buy crude on a netback basis protect themselves from the falling prices. The margin is locked in.

Refiners at the port of Corpus Christi, Tex., enjoy special treatment on duties and tariffs because they are in a free trade zone (OGJ, Dec. 16, 1985, p. 69).

That means they pay no duty or tariff on what they use or lose in processing, and their payments on finished products are made 3-4 weeks after the feedstock arrives, giving them the use of that money for a longer period than their competitors elsewhere on the Gulf Coast.

Refiners who account for their inventories on a last-in, first out (LIFO) method face another disincentive to cutting stocks.

A crude price drop to below a company's base LIFO reserve level reduces the cost of sales and boosts gross profit. And that means a larger figure on which to pay taxes.

One PADD III refiner that uses jobbers to market its products says of the January price drop, "We were caught with an inventory level that was higher than o[illegible] base LIFO layer. So we did lose som[illegible]

"Fortunately, we had a substantial reserve that prevented us from taking as big a hit as we might have. As we buy crude right now, we're hedging with the sale of products based on the yield we get in the refineries.

"We're trying keep a minimium operating level that's higher than our cheap LIFO layer."

**A job description.** Supply and distribution managers are pursuing two related objectives: turning their tanks more quickly and cutting product inventories.

To that end refiners are testing their supply and distribution networks for redundancies, shortening their supply lines, and developing techniques for obtaining nearly instant data on what they have and where they have it.

Some refiners are getting a premium for selling prompt product barrels.

One Gulf Coast refiner says that premium "is being paid by pipelines like the Colonial pipeline because they are paying you for holding those barrels. You are taking the risk, and they've got a deal locked up."

Companies also are cutting runs at their plants in the face of lower product prices and rapidly falling acquisition costs. Amoco Oil Corp. reduced crude runs at its refineries by about 50,000 b/d last month. Among other companies also cutting runs are Conoco Inc. and Citgo Petroleum Corp. (OGJ, Jan. 27, p. 52).

Planning this year will be difficult, especially for companies that produce large volumes of equity crude and market across a wide area.

"Planning is extremely difficult in view of the rapidly changing price scenario," says John Valesano, manager of light oils, supply planning, and optimization for Amoco Oil Corp.

"We're responding in two ways to manage our purchasing plans. The difficulty is projecting whether to run crude or buy product."

**The easy part.** Refiners have lowered inventories in a variety of ways besides directly reducing levels.

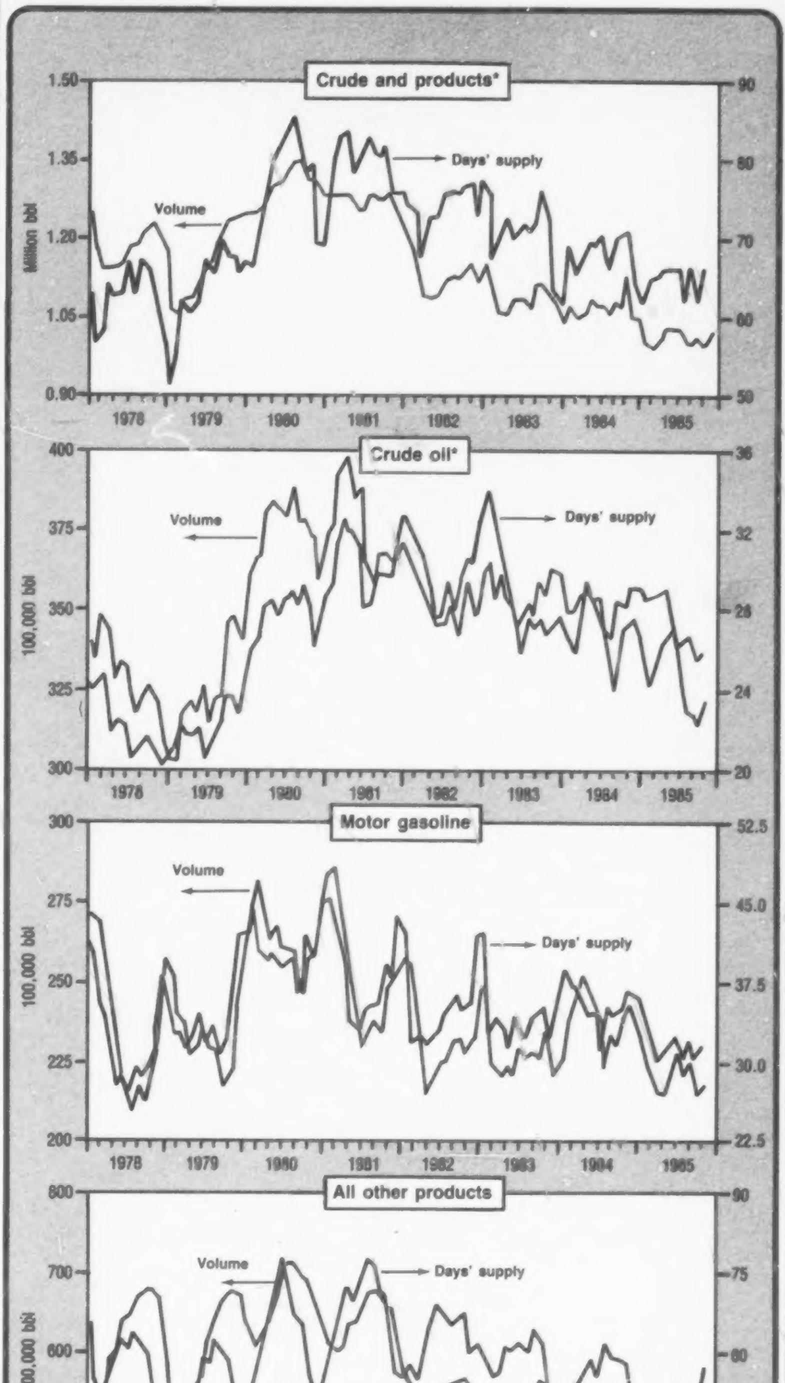
Many of last year's acquisitions and divestitures enabled refiners to lower product levels.

By swapping service stations and related assets like terminals, refiners are able to withdraw from areas with poor market share and concentrate on areas with good market share.

That, in turn, lowers unit distribution costs and creates opportunities to close redundant terminals within particular market areas (OGJ, Sept. 16, 1985, p. 57).

Likewise, refinery closures have allowed companies to carry less crude, intermediates, and product. And that means more working capital available for the company.

## How U.S. inventories have changed



*Excludes Strategic Petroleum Reserve.
Source: Energy Information Administration via Oil & Gas Journal Energy Database

OGJ

Closing or selling tankage is the easiest way to reduce inventories. The remaining cuts come more slowly and at greater cost.

**Getting help.** One theory of inventory reduction says that stocks are merely replaced with information about one's industry. To get that information, refiners are going to computer-based systems.

One means of keeping tabs on the overall movement of crude and products is through exchanges, like General Electric Information Services Co.'s Petroleum Data Exchange System.

The system's initial service, called the Refined Product Bill of Lading Exchange (Petroex), was introduced in 1974 and has grown to about 100 oil companies listed as subscribers.

Last December alone, GE's Petroex tracked 650,000 product transactions.

Besides using exchanges and networks, refiners use linear programs and simulation models to identify ways to reduce inventories.

Pace integrated a traditional refinery linear program with broader simulation models for a client, says Matson.

And that produced a dramatic reduction in that client's volume of inventory.

"We've seen a client go from 2-5 weeks (supply on hand) down to 10 days for the inventory for which he has responsibility," he says.

**Monitoring products.** Most of industry's attention is focused on finding more cuts in product stocks That means refiners are learning more about their own operations.

"Product inventory is the one that requires more monitoring," says Donald G. Miller, manager of refinery planning for American Petrofina Co. of Texas.

The company has a jobber system with about 100 terminals. "It's almost only at the end of the month when you find out what you have," Miller says.

"If we see we have less product moving out through our product system and we're still producing at the same level, that means we have to sell more product on the spot market."

Valesano says Amoco, which has reduced operating inventories 26% since 1980, is more closely monitoring product inventories at terminals "to be sure we don't have some spots in our inventory where inventory turns are substandard.

"You wouldn't want to send a year's supply to some terminal. You couldn't justify leaving it that long."

Amoco has launched a computer-based monitoring system that will keep tabs on inventory. The system, designed primarily for products, will be fully operational this year.

"Right now we have a widespread product distribution system, and that's our main focus: how to rationalize it and how to get the information on where you stand at all times."

In mid-1985 Placid Refining Co., Dallas, identified the minimum amount of finished product that it could maintain at its 46,000 b/cd Port Allen, La., plant and in its wholesale distribution system without running an unacceptable risk of product outages, says Larry K. Doty, general manager of refining.

"We worked diligently to maintain our end-of-the-month inventories as closely as possible to the level.

"If we see during the course of the month that our wholesale rack sales are not moving as much volume as we anticipated and our inventories are increasing over target levels, then we will sell spot product if we feel like there is no advantage to us to retain that product in storage.

"If we anticipate the spot price in the following month to be less than the current spot price, we will sell it. Historically, the wholesale rack has been a better market than the spot market."

**The hard part.** Refiners that have invested in computer-based systems to guide them or at least provide data are finding the process of implementing inventory cuts neither tidy nor logical.

"The method is quite unscientific," says an inventory manager for Mobil Oil Corp. "Sometimes those computers will tell you some goofy things.

"The big cuts have come not through any colossal enlightenment. It mostly has been keeping the pressure on. If once every 3 or 4 months you cut a refinery run for a few hours or even a day, you're just about in the right place."

Refineries tend to run whatever crude is available, he points out. "By pinching the valves off, we deliberately keep them on the lean side so they can't overrun.

"When you finally get to the point of running out at the terminals and supply folks are working hard to cover periodic tight spots by borrowing crude or time-trading one way or the other then you know you're close to where you ought to be."

**Supply time critical.** Use of domestic crudes instead of imported crudes cuts a refiner's supply time and, therefore, allows him to carry less inventory.

Among the largest oil companies citing the value of North American crudes as a means to smaller inventories are Mobil Oil and Phillips 66 Co.

American Petrofina's Miller says the company's 60/000 b/sd Big Spring, Tex., refinery keeps inventories, as measured by crude run days, very low because it uses much crude from nearby gathering systems.

The job of handling crude supply at the company's 90,000 b/cd Port Arthur, Tex., refinery is more difficult.

"If we're running foreign crude, we run a risk that one of the tankers could get fog-bound for a week," he says. "So we tend to run a higher inventory level if we run offshore crude. The biggest part of minimizing inventory involves scheduling.

"Rather than scheduling three ships at the first of the month, we try to schedule one at the first of the month, one in the middle of the month, and one near the end of the month."

Placid's refinery may carry one of the lowest days' crude supply of any U.S. refiner. The reason is that the company can run domestic crudes that arrive by pipeline rather than run offshore crude that arrives by tanker, says Doty.

"We have intentionally lowered the amount of crude oil we end the month with. We have an easier time since we're connected to the Exxon South Line system.

"We have probably reduced crude stocks by 100,000 bbl out of a total crude tankage of about 1.2 million bbl. We put crude inventories down to about 230,000 bbl. When you back out the heels of the tank, you're left with about 100,000 bbl of crude or about 2 days of run time. That gets us to about the minimum that we can safely operate on."

Refiners unable to increase direct use of close-in crude or far from their markets may be able to reduce their supply lines and, therefore, inventories by location trades (see p. 20).

**The outlook.** The level of crude stocks is not expected to decline much, if at all, says Pace's Matson.

"But with product inventories, there may be a fair amount of room to go down, and there will be a lot of angling to get someone else to own those inventories."

A Phillips 66 official says stock withdrawals may slow as traders begin expecting an end in the current price slide.

"Now the futures market price is not that different from the current month price. So there is probably not as great an incentive to cut inventories as there was last year.

"I just think you're getting to the point where the possibility of the prices going up is greater than the possibility of the price going down further. That doesn't mean, on the other hand, that it gives you any incentive to carry more inventory." ▪

# Volatility limits pose serious problems

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Table 1

Volatility trends of leaded gasolines 1960-1970

| | Rvp, psi | | | | | |
|---|---|---|---|---|---|---|
| | Regular | | Premium | | (R + M)/2 ON | |
| Year | Summer | Winter | Summer | Winter | Reg. | Prem. |
| 1960 | 8.7 | — | 8.8 | — | 87.9 | 94.4 |
| 1961 | 8.8 | 11.4 | 8.9 | 11.3 | 88.1 | 94.6 |
| 1962 | 8.9 | 11.5 | 8.9 | 11.3 | 88.3 | 94.7 |
| 1963 | 8.9 | 11.5 | 8.9 | 11.5 | 88.6 | 94.8 |
| 1964 | 8.9 | 11.6 | 9.0 | 11.6 | 88.8 | 95.1 |
| 1965 | 9.0 | 11.6 | 9.1 | 11.7 | 89.1 | 95.3 |
| 1966 | 9.0 | 11.7 | 9.0 | 11.9 | 89.3 | 95.5 |
| 1967 | 9.1 | 11.8 | 9.1 | 11.8 | 89.8 | 95.6 |
| 1968 | 9.1 | 12.0 | 9.2 | 12.1 | 89.9 | 95.8 |
| 1969 | 9.1 | 12.1 | 9.2 | 12.2 | 90.0 | 95.9 |
| 1970 | — | 12.1 | — | 12.1 | 90.1 | 96.0 |

* Reference 1

Gasoline volatility limits will cause serious problems in the near term for petroleum refiners. Refinery operations have increasingly generated more light material with the shift from lead antiknocks to processing to meet gasoline pool octane requirements.

The burden to solve these problems will fall on the petroleum industry to commit capital for condensation processes to convert the excess light material to gasoline.

Adequate time for orderly process revamps would lessen the economic impact, but the end result could be a higher price for gasoline relative to the cost of crude oil. The seriousness of the situation is verified by trends that show a steady rise in the volatility of gasoline reaching the marketplace.

The basic problem relates to an increasing imbalance between conversion and condensation processes. Butanes generated in petroleum refining are traditionally blended to gasoline or used as feed for condensation or petrochemical operations. Additional normal butane (n-butane, $nC_4$) purchased from natural gas processors is also absorbed in gasoline.

The increasing surplus of light ends, symbolized by $nC_4$, the "swing hydrocarbon" for volatility control, is being absorbed in the gasoline pool. The economic incentive in 1985 to absorb butane in gasoline ranges from 10 to 35¢/gal of butane, depending on geography and season. The octane incentive is equally attractive and, as a gasoline component, butane is several blend numbers above regular unleaded gasoline.

Oxygenates, primarily ethanol and methanol/cosolvent mixtures, have excellent octane-blending values and are being used in growing volume because of favorable economics. However, alcohols complicate volatility blending.

The Environmental Protection Agency (EPA) is studying gasoline volatility from the standpoint of hydrocarbon emissions as well as reviewing earlier waivers for oxygenate blending. Tightening of specifications beyond the traditional ASTM D 439 guidelines would place economic pressure on refiners, fuel-alcohol manufacturers, and gas processors.

**Volatility trends.** In order to appreciate the relationship between lead antiknock removal and gasoline volatility, a starting point is a historical review of octane and Rvp (Reid vapor pressure) trends. During the period 1960 to 1970, the octane quality of both premium and regular gasolines increased gradually and steadily as shown in Table 1. Both grades were leaded gasolines, and during the same period Rvp increased on a parallel trend.[1]

It was a time when vehicle manufacturers were still increasing compression ratio and petroleum refiners were responding with increased octane quality. The average compression ratio of U.S. cars increased from 9.0 to 9.5 and octane quality moved up nearly 2 numbers.

Petroleum refiners generated the additional octane quality from three major sources: increased lead antiknock concentration, more severe processing, and increased butane content of gasoline.

Several key factors encouraged the use of more butane in blending:

- The value of butane was lower than gasoline.
- More severe processing to improve octane generated more butanes.
- The octane quality of butane in gasoline with 1 g/gal lead is well over 100 (R + M)/2.

The trends of the 1970s were distorted by shortages and the oil embargo of 1973. Unleaded gasoline was introduced in the mid-1970s, and by 1979 began to exert octane pressure on the gasoline pool.

The U.S. clear-pool octane increased steadily. But some pressure was temporarily relieved by the drop in octane specifications for leaded gasoline during the 1979 shortage period. Further, the specifications for unleaded gasoline were set lower than those for the marketed leaded grade; 87 octane number (ON) vs. 88.

By 1980, a gradual and growing demand for an unleaded premium gasoline emerged, and from this point forward there was increasing pressure for more clear octane in the total gasoline pool. The parallel increase in gasoline volatility resumed with an upward movement of Rvp. Table 2 shows this trend for both the regular and premium unleaded grades from 1979 forward.[2]

The reasons for the current trends to greater gasoline volatility are similar to those of the 1970s, with the introduction of some new factors.

Butane-gasoline economics are still a key factor. Octane quality of n-butane is several numbers above unleaded regular. Processing severity has increased to meet the recent Jan. 1, 1986, limitation on lead antiknocks plus the increasing pressure from a diminishing leaded gasoline pool.

And finally, the growing use of alcohols as blending agents continues to increase gasoline volatility, mostly downstream of the refinery.

**Conversion effects.** Two basic refining processes account for almost 70% of the gasoline manufactured in the U.S.: fluid catalytic cracking (FCC) and the naphtha reforming. Both units have been stressed to generate octane quality. As a result, more light hydrocarbons are generated.

Light ends generated in the reformer are easily and directly measured. The function of the unit is strictly for octane improvement, and the production of light material can be equated directly against severity of operation.

Operation for higher octane in both FCC and reforming requires more energy in terms of heat input to the unit,

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Based on a paper presented at the National Petroleum Refiners Association annual meeting, Los Angeles, Mar. 23-25.

Table 2

## Volatility of unleaded gasoline, 1979-1985

| Year | Rvp, psi | | | |
|---|---|---|---|---|
| | Regular | | Premium | |
| | Winter | Summer | Winter | Summer |
| 1979 | 12.5 | — | 12.3 | — |
| 1980 | 12.7 | 9.8 | 12.7 | 9.9 |
| 1981 | 13.1 | 9.9 | 12.8 | 9.8 |
| 1982 | 13.5 | 10.3 | 13.1 | 10.2 |
| 1983 | 13.5 | 10.4 | 13.1 | 10.4 |
| 1984 | 13.5 | 10.2 | 13.1 | 10.3 |

Table 3

## Typical refinery gasoline components

| | FCC | Reformate | Alkylate | LSR | Light hydrocracked |
|---|---|---|---|---|---|
| Gravity, °API | 59.7 | 47.4 | 71.6 | 75.2 | 83.0 |
| Rvp | 7.2 | 7.7 | 5.1 | 12.0 | 14.3 |
| **ASTM distillation** | | | | | |
| IBP | 100 | 96 | 118 | 96 | 90 |
| 10 Evap. | 133 | 159 | 164 | 114 | 99 |
| 50 Evap. | 218 | 273 | 212 | 166 | 122 |
| 90 Evap. | 350 | 341 | 235 | 209 | 172 |
| EP | 408 | 417 | 282 | 238 | 204 |
| **Octane number** | | | | | |
| RON | 93.0 | 95.6 | 94.3 | 65.4 | 87.4 |
| MON | 80.0 | 86.1 | 92.2 | 65.1 | 84.3 |

and reduces liquid yield because of molecular rearrangement and fragmentation. Yields of hydrogen, methane, ethane, propane, and butanes all increase.

Another process, isomerization, has the potential to further increase the volatility of the gasoline pool. While the impact is less than either the FCC unit or the naphtha reformer, the process generates octane by conversion of normal compounds to isomers and therefore increases overall volatility.

**$C_4$/$C_5$ hydrocarbons.** Butanes occur naturally in crude oil. They are recovered as by-products from natural gas production. They are formed in the fluid cat cracker, the naphtha reformer, and the hydrocracker in the refinery. They are also formed in the steam-cracking process for ethylene manufacture.

Refinery operations, depending on the specific situation, leave a certain amount of butane in key streams such as light straight run (LSR), reformate, etc. In other words, gasoline streams are controlled by unit operations with a given Rvp, which can be as low as 0 to 1 psi for a heavy reformate or raffinate from aromatics extraction, to as high as 10 to 20 psi for LSR.

FCC gasoline is generally reduced in vapor pressure to the 7 to 8 psi range. This removes much of the butane cut, which is highly olefinic, for further processing (e.g., feed to alkylation, polymerization, etc.).

Table 3 is a list of key refinery components showing typical inspections including Rvp and ASTM distillation. Table 4 shows inspections of special refinery gasoline components.

Various gasoline components including a butane stream are blended to finished grades of gasoline. The amount of butane added depends on seasonal specifications.

The particular composition of the butane stream used for pressurizing varies and can be mixtures of $C_4$ hydrocarbons with different vapor pressures. Table 5 lists butane-hydrocarbons with different vapor pressures and octane qualities. However, because all butanes other than n-butane are potential charge stock for further processing, most refiners use $nC_4$ for vapor pressure control.

For winter specifications, refinery butane supplies for gasoline blending may be insufficient. Additional $nC_4$ may be purchased from sources outside the refinery, and in the Gulf Coast area, much of this butane is derived from natural gas liquids recovery.

In 1984, 74 million bbl (202,740 b/cd) of normal butane and 36 million bbl (98,630 b/cd) of isobutane were derived from natural gas processing. Essentially all of these butanes went to petroleum refining—the normal product for gasoline blending, the isomer for alkylation feed.

In addition, in 1984, there were 23 million (63,000 b/cd) more barrels of n-butane on the open market from refinery sources.[4] This product simply moved from refineries with excess butanes to refineries deficient in pressurizing agents for finished gasoline. Another point of use was for gasoline blending operations downstream of the refinery.

All of the butanes listed in Table 5 except n-butane have immediate, internal value in most refining complexes as feed for condensation and petrochemical operations. When internal unsaturated butanes are generated in excess of processing needs, they also can move to gasoline blending and replace purchased n-butane.

A situation such as this, on an industry basis, would soften the market for n-butane derived from natural gas liquids. It would also provide economic pressure for refiners to maximize butanes in finished gasoline to the extent specifications would allow.

In 1985, n-butane prices fluctuated from 50¢/gal to 63¢/gal. The lowest price generally occurs in the second and third quarters when gasoline is blended to summer specifications.

Lower priced n-butane in the marketplace also increases the incentive for maximum volatility of gasolines reblended downstream of the refinery gate. In the past, much of this operation involved leaded gasoline.

Today, a growing volume involves reblending of unleaded gasoline with alcohols—or complete reblending of unleaded gasoline with the addition of special components and more butane.

Table 5 also lists Rvp and octane quality of some of the $C_5$ and $C_6$ hydrocarbons. Generally, they are retained in refinery-gasoline streams unless there is a special petrochemical demand for these hydrocarbons.

For example, $C_5$ hydrocarbons were retained in the FCC gasoline and reformate of Table 3 and contributed a significant part of the Rvp of the stream. Table 4 shows a mixed pentane-pentene stream that has been segregated from cracked gasoline, possibly to improve octane and vapor pressure flexibility of gasoline blending operations. The stream also could have been segregated as petrochemical feed.

In the future, there may be a greater incentive to separate unsaturated $C_5$ hydrocarbons for further processing.

**Oxygenates.** The oxygenates, particularly the alcohols, add to the volatility problems in gasoline blending. They have excellent octane blending values, are being used in growing volume because of favorable economics, but are somewhat controversial in many quarters of the petroleum and automotive industry.

Recently, EPA has taken a more conservative approach with respect to alcohol waivers because of evaporative emissions. In any case, the alcohols are here to stay with respect to transportation fuel. Today they have an economic foothold and long term

Table 4

## Special refinery gasoline components

| | Heavy refmormate | Raffinate | Mixed pentanes | Arómatics |
|---|---|---|---|---|
| Gravity, °API | 37.7 | 72.2 | 74.9 | 30.6 |
| Rvp | 1.0 | 4.2 | 20.9 | 0.1 |
| **ASTM distillation** | | | | |
| IBP | 230 | 158 | 82 | 320 |
| 10% evap | 250 | 169 | 85 | 324 |
| 50% evap | 368 | 183 | 99 | 327 |
| 90% evap | 307 | 220 | 122 | 335 |
| EP | 374 | 312 | 360 | 355 |
| **Octane number** | | | | |
| RON | 100.8 | 57.5 | 95.4 | 109.6 |
| MON | 90.3 | 57.0 | 78.0 | 98.6 |

Table 5

## Rvp and octane number of light hydrocarbons

| | Rvp, psi | RON | MON | (R+M)/2 |
|---|---|---|---|---|
| n-butane | 52.0 | 94.5 | 89.6 | 92.0 |
| Isobutane | 71.0 | 100.3 | 97.6 | 98.9 |
| Isobutylene | 63.0 | 103.1 | 88.1 | 95.6 |
| 1-butene | 62.0 | 97.5 | 79.9 | 88.7 |
| 2-butene | 51.0 | 99.6 | 86.5 | 93.0 |
| n-pentane | 15.6 | 61.7 | 63.2 | 62.5 |
| Isopentane | 20.4 | 92.3 | 90.3 | 91.3 |
| Cyclopentane | 9.9 | 101.3 | 85.0 | 93.1 |
| 1-pentene | 16.0 | 90.9 | 77.1 | 84.0 |
| 2-methyl-2-butene | 15.0+ | 97.6 | 84.7 | 71.1 |
| 2,2 dimethyl butane | 9.9 | 92.3 | 92.9 | 92.6 |
| 2,3 dimethyl butane | 7.4 | 103.5 | 94.3 | 98.9 |
| n-hexane | 5.0 | 25.0 | 26.0 | 29.5 |

hey represent an alternative to hydrocarbons derived from crude oil.

Table 6 illustrates the value of oxygenates as octane improvers in unleaded gasoline.[5] Their disadvantage with respect to Rvp-blending value also is apparent (toluene and n-butane are included in the table for comparative purposes).

Is is obvious that the inclusion of an alcohol in gasoline will reject butane, assuming Rvp limits are to be maintained. The exception is gasohol, which contains 10% ethanol on top of specification gasoline, and according to law, does not require volatility adjustment. When an alcohol is added to gasoline, in sufficient quantity to categorize it as a blending component, the basic rules for predicting finished fuel volatility no longer apply. In other words, the vapor forming characteristics of an alcohol-hydrocarbon mixture cannot be defined by the same rules that apply to mixtures of hydrocarbons.

ASTM specification D 439 for gasoline does not recognize the existence of alcohol-gasoline blends. However, new specifications have been proposed. Nevertheless, alcohol-gasoline blends have been successfully marketed to the motoring public. These fuels have been carefully blended based on understanding of the differences between volatility aspects of alcohol-hydrocarbon products and 100% hydrocarbon fuels.

The key to satisfactory finished fuels blended with alcohol is based on methods to predict volatility specifications. Two common test procedures are involved: ASTM distillation and Reid vapor pressure.

The ASTM distillation curve is significantly changed by addition of an alcohol. Part of the effect is simply due to the addition of a lower-boiling component. For example, ethanol with a boiling point near 170° F. tends to flatten the curve in that area. Another effect, important to vapor formation of the mixture at temperatures below 170° F., is due to azeotropism.

An azeotrope is a mixture of two or more liquid compounds whose boiling point does not change as vapor is generated and removed. Because gasoline contains many different hydrocarbons, ethanol can form several azeotropes in the critical distillation range. The effect of an alcohol on the vapor pressure of gasoline is very pronounced even with the addition of small amounts.

Vapor pressure rises sharply up to the 3% concentration range, then levels off. Additional alcohol does not increase vapor pressure significantly.

Most volatility blending values and indices are based on ASTM distillation and Rvp. However, the temperature for a vapor/liquid ratio of 20 (T@V/L = 20) has been a recognized test method to indicate the tendency of a gasoline to cause vehicle-vapor lock.

The current test method calls for the use of ethylene glycol to interface with the gasoline sample in the test apparatus. However, ethylene glycol will absorb alcohol from an alcohol-hydrocarbon blend and cause incorrect results. The current recommendation for protecting alcohol-gasoline blends from vapor lock is to specify Rvp along with a minimum of 50% evaporated ASTM distillation limit.

Eventually the problems of alcohol-gasoline blends associated with volatility will be simplified. In the interim, extra care should be taken to compensate for the volatility effects of adding alcohols to gasoline. A careful approach to the final product can achieve both the octane increase and economic benefit of an alcohol component without the risk of negative reaction from the motoring public.

**Oxygenate limits, waivers.** Table 7 summarizes the oxygenate limits in unleaded gasoline as set by various EPA waivers. A discussion of the Petrocoal and Du Pont waivers is necessary background in order to understand some of the current EPA thinking about gasoline volatility.

The Petrocoal waiver[6] has been the most controversial waiver related to the use of alcohols as gasoline components. In 1985, the U.S. Court of Appeals for the Washington, D.C. Circuit cancelled the waiver and remanded the issue to EPA for further consideration. The basis for the court's decision was the failure of the Deterioration Emission Test for nitrogen oxide ($NO_x$).

According to the waiver "Petrocoal consists of up to 12 vol % methanol, up to 6 vol % of certain four-carbon alcohols in the presence of a proprietary inhibitor—for unleaded gasoline." Further, "the concentration of methanol does not exceed 15 vol %, the ratio of methanol to four-carbon alcohols in the finished fuel does not exceed 6.5 to 1, by volume ..." Therefore, Petrocoal fuel blended with 12% methanol plus cosolvent could contain more than 6 wt % oxygen.

A discussion of the relationship between oxygen content and exhaust emissions is needed for a partial understanding of why the Petrocoal waiver is under pressure.

In general, the addition of oxygen to gasoline by blending alcohol or any other oxygenate, will tend to reduce hydrocarbon (H) and carbon monoxide (CO) emissions. The stoichiometric air-fuel ratios for the combustion of oxygenates are lower than they are for gasoline. The effect is similar to reducing the amount of the fuel in the intake charge because the engine is carbureted for gasoline combustion. In other words, there is a "leaning" of the intake charge.

In the range of the oxygen contents under discussion, this almost always causes carbon monoxide (CO) emissions to decrease. Much of the reduction for CO emissions with gasoline-alcohol fuels can be explained on the basis of stoichiometrics.

On the other hand, hydrocarbon emissions can decrease, stay the same, or increase. Based simply on stoichiometrics, hydrocarbon emissions would also decrease.

However, other factors are involved such as fuel energy content, individual engine combustion temperature, and the change in detonation characteristics of the fuel. Using the same "leaning effect" argument, nitrogen oxides will increase. Undoubtedly, this is one major concern within EPA regarding the Petrocoal waiver.

By contrast, the DuPont waiver,[7] which was approved by EPA on Jan. 14, 1985, requires that the oxygen content of the alcohol-gasoline fuel is specifically restricted to a maximum of 3.7 wt %.

While the court seized upon the exhaust emission issue as the basis for cancelling the Petrocoal waiver, EPA is also concerned about evaporative emissions and the relation to unleaded-fuel volatility. In waivers prior to the Du Pont waiver, EPA relied on adherence to ASTM D 439 volatility specifications in order to control evaporative emissions.

For example, wording from the Federal Register in 1981 on the Petrocoal waiver was as follows:

"Thus, controlling the volatility of Petrocoal with ASTM volatility specifications should adequately control evaporative emissions and they should be no worse than those of commercially available fuels. It would be discriminatory to require the applicants' fuel to meet a more stringent volatility limit..."

In the Du Pont waiver, EPA made reference to the Petrocoal waiver and took an entirely new position:

"However, in a proposed revocation of one of these waivers, the Agency found that new information demonstrated that adherence to the ASTM standards was not sufficient to ensure compliance with evaporative emissions standards."

Table 6

## Blending values of oxygenates in typical unleaded gasoline[5]

| | Octane (R + M)/2 | Reid vapor pressure B.V.* | Reid vapor pressure Rvp increase |
|---|---|---|---|
| Methanol | 116 | 61.0 | 3.0 |
| Ethanol | 113 | 21.5 | 0.7 |
| Arconol | 98 | 12.7 | 0.3 |
| Oxinol 50 | 107 | 33.5 | 2.0 |
| MTBE | 106 | 9.3 | — |
| n-butane | 92 | 60.0 | — |
| Toluene | 106 | 0.5 | — |

* Blending values vary depending on gasoline hydrocarbon type and exact composition of the oxygenate. For methanol and ethanol, it is more accurate to use Rvp increase unless values have been developed for specific fuels.

Table 7

## Oxygenate limits in unleaded gasoline

| | Maximum | | |
|---|---|---|---|
| Oxygenate | Oxygen, wt % | vol % | Oxygenate date |
| General rule (methanol excluded) | 2.0 | — | 10/10/80 and 7/28/81 |
| Equal volumes of methanol and $C_4$ or higher molecular weight alcohols | — | 3.5 | 7/28/81 |
| MTBE | 2.0 | 11.0 | General rule 10/5/81 |
| Petrocoal | | | |
| Methanol-$C_4$ alcohol ratio equal or less than 6.5 | — | 15.0 | |
| Methanol maximum | — | 12.0 | |
| Oxinol up to 50% methanol in GTBA | 3.5 | — | 11/16/81 |
| Oxinol 50 (50% methanol and 50% GTBA) | 3.5 | 9.6 | 11/16/81 |
| GTBA (no methanol) | 3.5 | 16.0 | 11/16/81 |
| Gasohol (ethanol) | 3.7 | 10.0 | 4/5/82 |
| Du Pont | 3.7 | | 1/14/85 |
| Methanol, maximum | — | 5.0 | |
| Cosolvent, minimum (any one or mixture of ethanol, propanols, or butanols) | — | 2.5 | |
| Blends meet EI* | — | — | |

*EI = 0.85 Rvp + 0.14 (% evap @ 200° F.) − 0.32 (% evap @ 100° F.)

Research by automobile companies and others has shown that gasoline blends containing alcohols produce more hydrocarbon emissions in the SHED Test than blends without alcohols having the same vapor pressure and volatility index. Higher evaporative emissions of alcohol-gasoline mixtures, particularly for the lighter alcohols, are related to a unique volatility effect of the blend.

As pointed out earlier, the alcohol and gasoline singly will have lower vapor pressures than the combination of the two. Even though gasoline distillation specifications are adjusted in alcohol-gasoline blends to compensate for greater volatility, evaporative emissions may be higher.

The Du Pont waiver allows methanol and various cosolvent alcohols, but volatility limits are carefully controlled either by alcohol concentration limits or by light hydrocarbon rejection. Cosolvents for methanol can be any one or a mixture of ethanol, propanols, or butanols, including gasoline grade tertiary butyl alcohol (GTBA). The following conditions must be met by the refiner or blender responsible for the finished fuel:

- A maximum of 5 vol % methanol and a minimum of 2.5 vol % cosolvent.
- A maximum of 3.7 wt % oxygen in the final fuel.
- Corrosion inhibitor must be Du Pont's DGOI-100.
- ASTM D 439-83 standards must be met. The Rvp test is executed using the dry bomb procedure.
- Volatility specifications of the Evaporative Index— EI = 0.85 Rvp + 0.14 (% evap @ 200° F.) − 0.32 (% evap @ 100° F.).
- Final fuel will not be used as a base gasoline to blend additional oxygenates.

On the surface it might appear that ethanol will become attractive as a cosolvent for methanol. However, the volatility specification of the EI requires very careful control under the Schedule of Seasonal and Geographical Volatility Classes as defined by ASTM D 439. This greatly reduces the economic incentive for ethanol as a cosolvent. In the language of the Du Pont waiver, the EPA administrator interpreted the evaporative index as controlling evaporative emissions as follows:

"The three volatility measures which are added to form the EI are Rvp, percent evaporated at 100° F., and percent evaporated at 200° F. The first two are measures of fuel properties one can expect to be important in the generation of vapors from fuel tanks, since fuel tanks generally remain in a temperature range not exceeding about 100° F. The percentage evaporated at 200° F. should correlate with vapor generation in a fuel float bowl, since as engines are temperature controlled to about 200° F. during operation, this is approximately the temperature driving evaporation from the float bowl."

While the above reference relates to evaporative emission control, the volatility restrictions imposed by EI are an excellent safeguard against vehicle vapor lock. Therefore, EPA's waiver decision is carefully designed to avoid adverse market reaction from excess volatility.

There have been complaints that the evaporative index limit of the Du Pont waiver is too restrictive, and it is possible that the measure is an over reaction by EPA because of the history of volatility problems with alcohol-gasoline blends in the marketplace. Nevertheless, it is evident that EPA will continue to hold the line on the 3.7 wt % oxygen limit and will control volatility with measures that are more restrictive than ASTM D 439 in any future waivers for unleaded fuels containing alcohol.

The Agency will also look "over its shoulder" at previously granted waivers. It should be recognized that EPA has the authority to regulate the volatility of all gasoline.

**EPA posture.** The best indication of the likely EPA posture on gasoline volatility control may be taken from the abstract of the November 1985 Study of Gasoline Volatility and Hydrocarbon Emissions from Motor Vehicles.[8] Part of the abstract is quoted below:

"In-use motor vehicle evaporative hydrocarbon emissions greatly exceed their applicable EPA emission standards. The primary reason is that the volatility of commercial gasoline is substantially greater than that of the certification test fuel specified by EPA (i.e., vehicles are simply not designed to handle the fuel volatility they regularly experience.)

The long-term solution is to equate the volatilities of commercial and certification test gasolines. This can be done at: the current volatility of commercial gasoline, that of certification test gasoline, or at some point in between. However, in the short term, only the reduction of commercial gasoline volatility has a significant environmental benefit, since the effect of certification fuel modifications must await the turnover of the vehicle fleet..."

## The author...

**Unzelman**

George H. Unzelman is a fuel consultant in Fallbrook, Calif., specializing in hydrocarbons and oxygenates. Current interests include diesel-fuel blending, oxygenate blending into hydrocarbon fuels, and gasoline volatility. In January 1985, he formed HyOx Inc.

Unzelman was formerly technical director of the Petroleum Chemicals Division of Ethyl Corp., Baton Rouge, La Unzelman also spent 8 years with Continental Oil Co. before joining Ethyl in 1955. He is a member of AIChE, a past member of API's refining division, and he served on the operating practices, petroleum products, and program committees of API. He was also vice-chairman of the manufacturing committee of the National Petroleum Refiners Association, and served as program committee chairman for NPRA's 1982 and 1983 annual meetings.

**Economics.** It is beyond the scope of this article to independently determine the effect of vapor pressure restrictions on the cost of gasoline and on the butane market. The subject has been studied extensively for EPA by major consulting firms.

Bonner & Moore Management Science used its refinery and petrochemical modeling system[8] to estimate the nationwide average cost of vapor pressure reduction on gasoline. For alcohol-free blends representing almost 89% of gasoline sold in the U.S., costs to reduce gasoline Rvp by 1 psi are 0.62-0.85 ¢/gal; costs to reduce gasoline Rvp by 2 psi are 1.40-1.97 ¢/gal. Cost was greater for gasolines containing methanol and cosolvents. Cost for controlling gasohol was still under study. Jack Faucett Associates studied the effect on the butane market. The conclusion was that any significant reduction of gasoline vapor pressure would free enough normal butane to lower its market price to petrochemical value. It would then replace other feedstocks for manufacture of ethylene, acetic acid, etc.

An industry-type model tends to be a "blunt instrument" that establishes benchmarks rather than precise costs. The model generally has a degree of flexibility not duplicated in the real world and therefore can turn out optimistic numbers. For example, the differential between the cost of leaded and unleaded gasoline in the 1980 marketplace was not predicted in the 1970s from the results of modeling. Rather it was extrapolated from model results by those who understood the marketplace.

If stringent volatility restrictions are applied to alcohol-gasoline blends, the burden for controlling specifications will rest at the refinery level with sub-octane and sub-volatility gasolines. Controlling volatility requires sophisticated blending and testing facilities generally not available downstream of the refinery gate. This type of control would be an added cost factor for alcohol-gasoline blending.

To suggest that large quantities of normal butane rejected from gasoline would be absorbed as petrochemical feed without disrupting the total market is too simplistic. Other studies have indicated that low-octane pentane/hexanes from natural and straightrun gasolines also would be partially absorbed as feed for ethylene manufacture. The basic question arises, how much material can petrochemicals absorb?

The ultimate solution for rejected normal butane and low-octane pentane/hexane is not petrochemical feed. Rather, the burden lies with the petroleum refining sector itself.

Processing, which will include some new condensation technology, will be the key to return those components to the gasoline pool. Capital investment and a reasonable time frame for installation of new equipment is essential to prevent market disruption.

Obviously, the price of gasoline is determined by market forces. However, volatility restrictions requiring additional capital outlay and higher operating costs would eventually impact on the consumer.

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# Petrochemical Report

## Petrochemicals may fare better as feed costs dip and processes are improved

**Ted Wett**
Petrochemical/Gas Processing Editor

With fewer projects under way and with lower feedstock costs, the U.S. and European petrochemical industries could fare better this year.

According to a survey by the Chemical Manufacturers Association, chemical industry shipments were up nearly 3% in the U.S. in 1984, compared to a year earlier. However, basic petrochemical production did not share uniformly in that increase (Table 2).

Comparative polymer and aromatics output was on the positive side, as was output of acetic acid, acrylonitrile, and vinyl chloride. But production of many other materials, including ethylene and propylene, was lower than the year before.

The drop in ethylene output is somewhat deceiving. Producers for the most part were running available capacity near the maximum. Demand held up well and inventories dropped throughout the year, falling from over 2 billion lb to about 970 million lb as of the end of December.

U.S. demand for ethylene and propylene is expected to remain strong in 1986. Propylene, in particular, should benefit from a worldwide shift to lighter feedstock.

Petrochemical demand was also strong worldwide, and U.S. exports were relatively good. The long term projection is for a drop in the U.S. balance of trade in petrochemicals for the rest of the decade. But 1985 saw mishaps at production facilities in Europe that actually prompted a healthy increase in imports from the U.S., particularly for high-density polyethylene.

Still, the International Trade Commission sees a drop in the U.S. petrochemical trade balance from the current $10 billion to around $1.6 billion in 1990 as a result of the expansion of the petrochemical industry in developing countries. Energy-rich nations will be exploiting their cost competitive position in world markets.

Falling oil prices have given European producers some breathing room, however.

One producer feels that European plants based on naphtha can, at least for a time, be competitive with the Middle East's ethane-fed plants, when delivery costs are factored in.

Table 1

## Global projects*

| | 1981 | 1984 | 1985 |
|---|---|---|---|
| North America | | | |
| Canada | 34 | 10 | 12 |
| United States | 60 | 19 | 17 |
| **Total** | **94** | **29** | **29** |
| Latin America | | | |
| Argentina | 18 | 19 | 23 |
| Bolivia | 15 | 3 | 2 |
| Brazil | 36 | 16 | 9 |
| Chile | — | 2 | 3 |
| Colombia | 5 | 1 | 1 |
| Ecuador | 3 | 3 | 3 |
| Mexico | 64 | 12 | 18 |
| Peru | 1 | — | — |
| Puerto Rico | — | — | — |
| Trinidad | 2 | 1 | 1 |
| Venezuela | — | — | — |
| **Total** | **86** | **57** | **61** |
| Asia/Pacific | | | |
| Australia | 7 | 1 | 2 |
| Burma | 1 | 3 | 3 |
| China | 31 | 25 | 28 |
| Hong Kong | — | — | — |
| India | 40 | 43 | 36 |
| Indonesia | 5 | 4 | 55 |
| Japan | 35 | 5 | 7 |
| Korea | 13 | 10 | 12 |
| Malaysia | — | — | — |
| New Zealand | 3 | — | — |
| Pakistan | 3 | — | — |
| Philippines | 2 | — | — |
| Singapore | 5 | — | — |
| Sri Lanka (Ceylon) | — | — | — |
| Taiwan | 28 | 6 | 5 |
| Thailand | 3 | 8 | 11 |
| **Total** | **176** | **107** | **110** |
| Western Europe | | | |
| Austria | 7 | — | 1 |
| Belgium | 3 | 1 | 2 |
| Denmark | — | — | — |
| Finland | — | 3 | — |
| France | 3 | 2 | 3 |
| Germany (West) | 9 | — | 3 |
| Ireland | — | — | — |
| Italy | 1 | 2 | 1 |
| Netherlands | 7 | 4 | 1 |
| Norway | — | — | — |
| Portugal | 11 | 1 | — |
| Spain | 21 | 8 | 5 |
| Sweden | 1 | — | — |
| U.K. | 7 | 1 | — |
| **Total** | **70** | **22** | **16** |
| Eastern Europe | | | |
| Bulgaria | 6 | 2 | 2 |
| Czecho-slovakia | 5 | 5 | 2 |
| Germany (East) | 3 | 1 | 2 |
| Greece | 4 | 1 | 3 |
| Hungary | 2 | 4 | 1 |
| Poland | 3 | 1 | 1 |
| Rumania | 27 | 4 | — |
| U.S.S.R. | 27 | 11 | 11 |
| Yugoslavia | 17 | 5 | 6 |
| **Total** | **94** | **34** | **28** |
| Middle East and Africa | | | |
| Bahrain | — | — | 2 |
| Bangladesh | — | — | 2 |
| Egypt | 3 | 6 | 5 |
| Iran | na† | 1 | 1 |
| Iraq | na | — | 1 |
| Israel | 3 | 3 | 2 |
| Jordan | 4 | — | — |
| Kuwait | 8 | 9 | 2 |
| Libya | 8 | 6 | 1 |
| Madagascar | 2 | — | — |
| Nigeria | 2 | 11 | 10 |
| Qatar | — | — | — |
| Rep. of S. Africa | 11 | 2 | 1 |
| Ras Al-Khaimah | — | 1 | 1 |
| Saudi Arabia | 19 | 6 | 7 |
| Sudan | 1 | — | — |
| Tanzania | 2 | — | — |
| Turkey | 23 | 4 | 3 |
| Others | 8 | 2 | — |
| **Total** | **93** | **50** | **38** |
| **World total** | **612** | **299** | **282** |

*For projects, all units are counted separately—either proposed, planned, or under construction. †Not available. Source: Petrochemicals—Worldwide.

**Long-term outlook.** In the long run, it appears inevitable that hydrocarbon-rich countries will be taking a greater share of worldwide petrochemical production. Saudi Arabia, Canada, Mexico, and others are building toward this future. But the plunge in oil prices, which could strap oil producing countries for cash, will probably delay any major expansions.

Capital expenditures for the chemical industry in the U.S. are expected to increase in 1986. However, it's generally accepted that basic petrochemicals will not be the prime outlet for these funds. Also, only about one-third of the money will be spent for new capacity.

Expenditures for environmental controls and other efforts to improve both the image and performance of companies in the field of safety will go up rather sharply. The Chemical Manufacturers Association estimates that 13% of capital expenditures by U.S. chemical companies will go for control of air and water quality, solid waste management, and occupational health. A year ago, the forecast was that only 7% would be spent for these purposes.

Two markets with anticipated growth potential are obvious from the list of planned projects (Table 1) in the OGJ construction survey: octane boosters and polymers. Worldwide, only the 30 ammonia projects are more numerous than the 22 listed for polyethylene. There are 14 ethylene projects, but most will be for debottlenecking, efficiency improvement, or feedstock flexibility.

Among the octane booster projects are those for methyl tertiary butyl ether (MTBE). There are 11 MTBE projects listed, and 10 for methanol.

Restructuring/rationalization is still proceeding in petrochemicals at a pace never seen before. Many unusual measures are being taken to adjust to slower market growth, maturing products, cost of government regulations, and foreign competition. Reorganizations, divestments, acquisitions, leveraged buyouts, stock buybacks, and personnel separations are a consequence of these efforts.

Cefic president, John Harvey-Jones, expects restructuring in Europe to go on at a high rate, and for investment in cost-cutting revamp projects to have a resurgence.

Better efficiency, less energy use, reduced raw material needs/unit of output, and feedstock flexibility are the targets of projects in plants making ammonia, urea, ethylene, and a variety of intermediates.

One method of reducing costs is to be as sure as possible that process design, control schemes, and operator performance are the best that they can be. Thanks to recent increases in computer power and a variety of software approaches, this job is not as difficult as it once was.

Dynamic process simulation is helping to both design processes and train the operators that will run them. Operator training on computer-based process simulators is helping speed and improve plant start-ups and reduce lost production time due to any upsets that do occur. Precise determination of the proper interaction of energy flows within a process is saving on utility costs. Pressure of competition from producers in low energy cost and feedstock-rich countries will continue to mount.

Although oil prices have sagged, the benefit isn't much help when the downstream customer expects an immediate pass through.

Profit margins didn't contribute many happy faces to petrochemical boardrooms in 1985.

But lower overall feedstock costs, if they persist, could lower product prices and promote further consumption in the buoyant U.S. economy.

U.S. prospects for 1986 are cloudy, with exports expected to stay flat or decrease. Profit margins will be hinged on the activity in the crude and gas liquids markets. ▪

Table 2

## U.S. production of selected petrochemicals

| | 1984 | *1985 |
|---|---|---|
| | — Million gal — | |
| Benzene | 1.339 | 1.349 |
| Toluene | 0.726 | 0.688 |
| Xylene | 0.850 | 0.738 |
| | — Million lb — | |
| Ethylene | 31.178 | 30.550 |
| Propylene | 15.470 | 14.977 |
| Butadiene | 2.531 | 2.525 |
| Cumene | 3.360 | 3.345 |
| Cyclohexane | 2.130 | 1.739 |
| Ethylbenzene | 8.613 | 8.548 |
| Phenol | 2.845 | 2.777 |
| Phthalic anhydride | 0.866 | 0.836 |
| Styrene | 7.706 | 7.454 |
| o-Xylene | 0.696 | 0.698 |
| p-Xylene | 4.268 | 4.669 |
| Polyethylene, | | |
| Low density | 8.159 | 8.346 |
| High density | 6.463 | 7.040 |
| Polypropylene | 4.961 | 5.180 |
| Polyvinyl chloride | 6.958 | 6.890 |
| Acetic acid | 2.642 | 2.875 |
| Acetone | 1.887 | 1.803 |
| Acrylonitrile | 2.201 | 2.346 |
| Ethylene glycol | 4.842 | 4.679 |
| Ethylene oxide | 5.985 | 5.833 |
| Formaldehyde | 5.712 | 5.701 |
| Ethylene dichloride | 13.731 | 13.635 |
| Vinyl chloride | 7.513 | 7.775 |
| Isopropyl alcohol | 1.146 | 1.118 |
| Maleic anhydride | 0.360 | 0.371 |
| Methanol | 8.279 | 5.979 |

*Preliminary. Source: U.S. International Trade Commission.

# Texas holds leading refining position in the U.S.

**Richard A. Corbett**
Refining Editor

Texas refining holds a strong position of leadership in the U.S. and the world. The state leads the nation in refining capacity and number of refineries, and can produce a complex product slate from widely varying feedstock quality.

When declining demand for oil products caused a steep decline in refining capacity in the U.S., Texas bore the brunt of the plunge in capacity and number of refineries. But it maintained its leading position.

The Texas industry has been that way for many years. As early as 1919, Texas led the nation in the volume of crude oil refined.

In addition to having the largest concentration of refineries and capacity in the U.S., Texas also has some of the most technologically advanced refineries in the world, a good number of which are coupled with worldscale petrochemical complexes. In fact, many of the existing technologies were first tried in Texas refineries.

The close association of refineries and basic petrochemical plants is the major reason Texas also holds a commanding lead in primary petrochemicals (Table 1).

**Today's picture.** Texas has seen a substantial share of its refining capacity disappear since the all-time high in refining capacity in 1980. Between Jan. 1, 1981, and Jan. 1, 1986, Texas shutdown 1,127,290 b/cd in crude charging capacity. That represents about 35% of the total U.S. capacity lost during the period. The number of refineries fell from 59 to 31 or 25% of the number of U.S. refineries closed. But Texas refiners have improved their efficiency and strengthened their downstream capability.

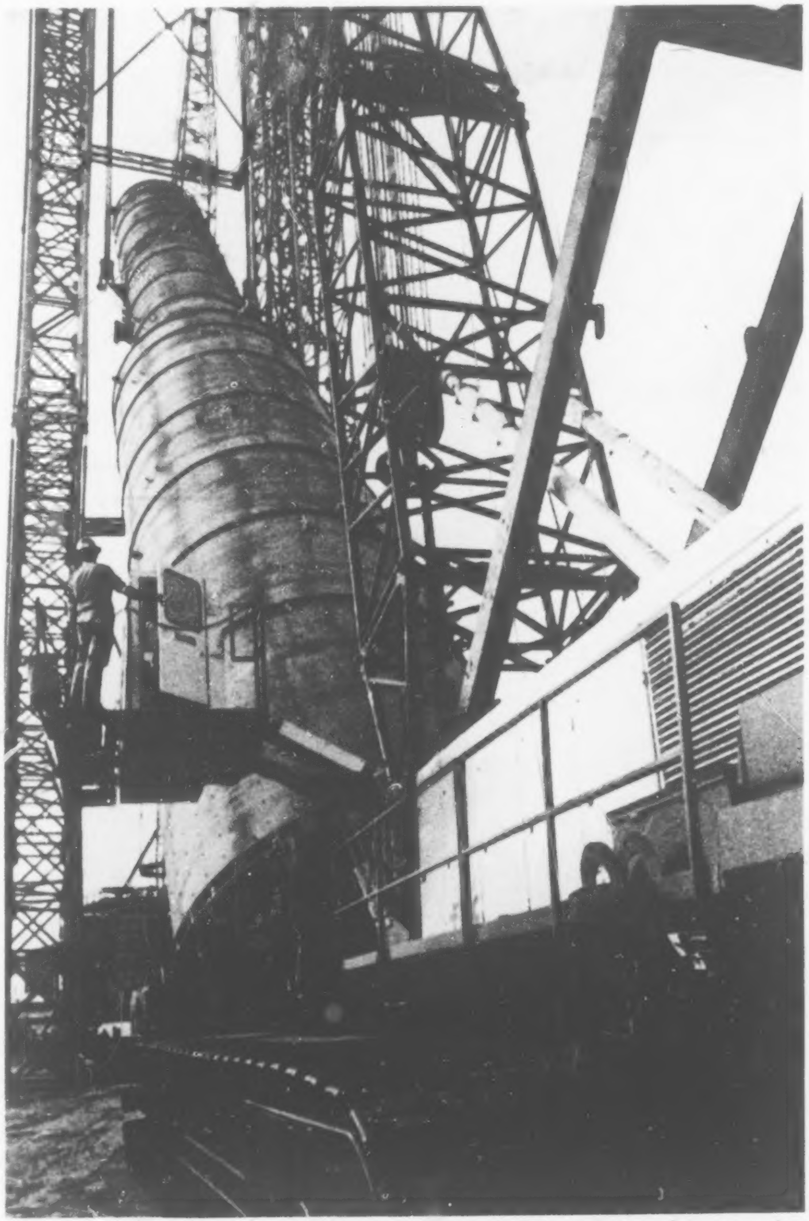
Texas still tops the U.S. in crude-charging capacity, ranking fourth worldwide. It is the home of the world's largest complex refinery—Exxon's Baytown facility. And it ranks high in downstream conversion capability, especially those processes for gasoline production.

This obviously makes Texas a prime market for world catalyst suppliers and other companies servicing the refining industry.

Capacity of catalytic cracking, the leading light fuels producing process, is 1,587,000 b/d in Texas. This is about 30% of the total U.S. cat cracking capacity and 17% of the world's capacity. It ranks third behind the rest of the world at 4,114,517 b/sd and the rest of the U.S. at 3,647,100 b/sd.

Texas also leads the nation with about 28% of the nation's catalytic reforming and alkylate production capacity. The combined capacity of these processes and catalytic cracking confirm Texas' leading position for gasoline supply.

Texas has a strong position in catalytic hydrorefining and hydrotreating. About 33% of the U.S capacity for both these processes is installed in the



**Reactor** vessel is lifted into place for Amoco's 22,000-b/d alkylation unit, under construction at the Texas City refinery.

Table 1

## Texas' share of primary petrochemicals capacity

| Product | Texas capacity | Total U.S. capacity | Percent |
|---|---|---|---|
| Benzene, million gal/year | 1325.7 | 2394.0 | 55.4 |
| Toluene, million gal/year | 826.0 | 1568.0 | 52.7 |
| Xylene, million gal/year | 785.0 | 1543.0 | 50.9 |
| MTBE, million lb/year | 3020.0 | 4105.0 | 73.6 |
| Cyclohexane, million gal/year | 332.6 | 359.3 | 92.6 |
| Ethylene, million lb/year | 24640.0 | 34645.0 | 71.1 |
| Propylene, million lb/year | 13029.2 | 22266.5 | 58.5 |
| Butadiene, million lb/year | 3519.0 | 3990.0 | 88.2 |
| Cumene, million lb/year | 2764.1 | 4047.6 | 68.3 |

Source: DeWitt & Co. Inc. and Debreczeni & Associates, members of the DeWitt Consulting Group.

state's refineries.

Texas is responsible for a big chunk of the nation's lubricant production capacity. Its 94,100 b/sd capacity is 40% of the total U.S. capacity.

Many Texas refineries, as noted, are part of a complete manufacturing complex including petrochemicals. Most of the major refineries, such as Exxon at Baytown, Shell at Deer Park, ARCO at Lyondell (all within 25 miles of downtown Houston, Texaco at Port Arthur, and Phillips at Sweeny, have petrochemicals complexes adjacent to their refineries. This close proximity gives Texas refineries and petrochemical complexes an advantage in feedstock and product slate flexibility.

Refineries and gas-processing plants are the primary source of feedstocks for olefins production, while almost all the aromatics are made within refineries.

**Early refining.** Texas' leading position in refining began in the early days of U.S. refining, its growth spurred by the discovery of oil at Spindletop, the East Texas fields, etc. The impetus for building refineries in Texas was based primarily upon the superior quality of Texas crude and the apparent certainty of an immense volume of it extended over a long time.

Back in 1919, what appears to be the first comprehensive refining report in OGJ was published—at least according to present records. Texas first gained its lead in refining that year.

There were 43 refineries in Texas, processing about 229,200 b/d of crude. This was about 19% of the total crude processed in the U.S. (1,208,708 b/d). The approximate investment in refining facilities ran at $98,129,000. Back then, refineries owned pipelines and tank cars. Texas refiners owned 6,125 miles of pipeline and 7,250 tank cars.

In addition to leading the nation in crude oil refined, and having some of the largest refineries operating, the future of refining in Texas looked bright. The OGJ refining report, dated May 30, 1919, remarked about the future of the oil industry in Texas:

"Within the next 3 to 5 years, Texas is liable to rank first in production, refining, and capital invested in oil. It may be a little early to make predictions, but it may safely be said all signs point that way now. It already ranks first in volume of crude refined."

The present situation in Texas certainly confirms those early, cautious projections. Texas refining has led the way ever since. Those early days were not without governmental interference either, as revealed by the 1919 report. To ward off an apparent gasoline shortage, the fuel administration restricted gasoline usage. But Texas refiners claimed there was no shortage, at least in their territory.

"And yet, with the industry everywhere satisfied there would be no shortage of gasoline, the fuel administration inaugurated gasless Sundays, and the New York Tribune says, 5 million automobile owners made heroic sacrifice. Of course, that 5 million was somewhat exaggerated, but whatever sacrifice was made was wholly uncalled for, if the men of the industry had known anything about their business," said the report.

**Feedstock flexibility.** The geography of the Texas refining industry shows a high concentration of its refineries on the Texas Gulf Coast. More than 60% of its refineries are located along the coastal strip between Port Arthur and Corpus Christi. This proximity to several sea ports makes a wide variety of the world's crude oils available from most of the world's shipping points.

An investigation of the various crudes that have been run in Texas refineries would reveal crudes ranging from heavy Mexican Maya and Venezuelan Bachaquero to lighter crudes like Saudi Arabian Light and Murban from Abu Dhabi. Even crudes from exotic places, Sarawak, Malaysia (Miri Light), and Kalimantan, Indonesia (Sanga Sanga), have found their way to Texas. In spite of Texas' leadership in crude oil production, just about all of the world's export crudes have, at one time or another, been processed in Texas.

It may seem that Texas reached this flexible position after the U.S began importing a large amount of its crude oil needs. But a look at history shows that Texas had a highly flexible position as early as 1919.

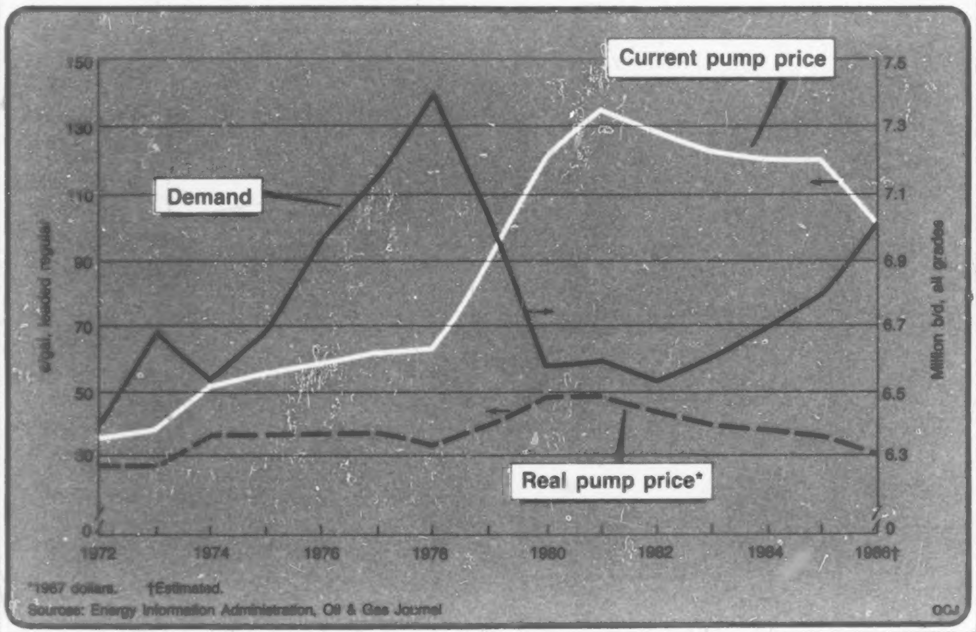
Imported crudes weren't important then, but the Gulf Coast location, particularly the Houston area, of many of the Texas refineries gave it an advantage over others as this quote from the early OGJ report states: "The Houston canal or ship channel offers exceptional facilities for large refineries and it now looks as if, in a little while, that waterway will outrank Bayonne (N.J.) in the number of its large petroleum manufacturing concerns, and its additional numbers may, in time, outrank Bayonne in the volume of crude treated. It will have the advantage of Bayonne of having fresh crude to handle, and it will have the immense advantage of having crude directly at its doors."

**Technologies.** A number of recent projects have kept the Texas industry at the leading edge of refining technology. Many of these projects confirm the industry's long-term commitment to handle the heavier, lower-quality crude oils and resids. And many of these projects also add to the olefins production capability for petrochemicals production. Examples of these projects are:

- Exxon's Baytown Resid Upgrading Project (BRUP) that uses Flexicoking to produce light fuels and eliminate low-value coke. Chargestocks will come from heavy Mexican and Californian crudes.
- Amoco's 60,000 b/d LC-Fining unit at Texas City to convert high-sulfur vacuum resid to cat cracker feed and other light products.
- Amoco's reformer revamp to an isomerization unit and the construction of a 22,000 b/d alkylation unit, both for production of high-octane gasoline components.
- AES Deepwater's 154,000-kw cogeneration facility that will supply steam to ARCO's Pasadena refinery. The cogeneration facility will use petroleum coke for fuel.
- Shell's coal gasification demonstration plant under construction at Deer Park that will allow Shell to study alternate fuels.
- Valero Refining Co.'s Corpus Christi refinery that is designed to process resids rather than raw crude oil.

These projects, and others for heavy oil conversion and gasoline octane ehancement, will keep Texas refiners in the leading position they have held for so many years. •

How U.S. gasoline demand and price compare



*1967 dollars. †Estimated.
Sources: Energy Information Administration, Oil & Gas Journal

# U.S. refiners see no problem meeting higher gasoline use

**Robert J. Beck,** Economics Editor
**Michael Obel,** Staff Writer

Continuing economic growth, strong vacation driving, and a sharp drop in the pump price of motor gasoline have boosted U.S. motor gasoline demand in first half 1986.

The Oil & Gas Journal estimates that 1986 demand through May 30 averaged 6.842 million b/d, up 2.2% from the same period a year ago.

The demand hike comes during a time of low gasoline stocks. Measured in days' supply, motor gasoline inventories at the start of the summer driving season have fallen to their lowest level in 10 years.

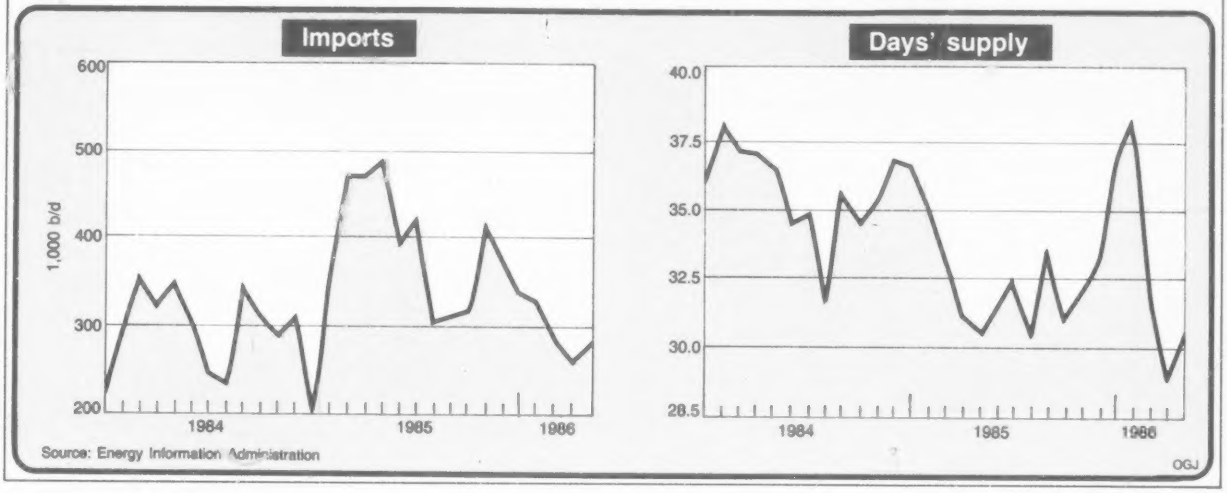
Refiners see no problem in meeting demand. In April and early May, however, a sharp drop in primary inventories caused some companies' marketers to worry.

But it appears that the first quarter demand hike—and resulting drawdown in primary gasoline inventories—resulted from jobbers' loading up bulk terminals to take advantage of big retail-rack price spreads.

In recent weeks imports of gasoline and blending components have picked up a bit, but they remain well below last year's volumes and are much closer to historic levels. The weakening of the U.S. dollar against certain currencies makes imports less attractive than they were in 1984 and early 1985, when gasoline imports rose.

If pump prices remain close to present levels for the remainder of the year the average U.S. pump price for 1986 will be about $1.02/gal.

How U.S. gasoline imports and inventories have varied



Source: Energy Information Administration

Adjusted for inflation, that would be 7.5% below the average pump prices of 1978 and the lowest level since 1973, the year of the first sharp price hike.

Meantime, sales of fuel ethanol are recovering from a dismal first quarter. Information Resources Inc. (IRI), Washington, D.C., says prices and sales increased in April and May.

**Demand up.** American Petroleum Institute estimates motor gasoline demand for the first 4 months of 1986 at 6.774 million b/d, up 2.6% over the same period in 1985. Demand for April was 7.127 million b/d, up 2.8%.

Demand is expected to remain strong throughout the summer driving season. Independent Petroleum Association of America's supply and demand committee forecasts 1986 demand at an average 7.05 million b/d vs. 6.815 million b/d in 1985.

IPAA's latest 1986 forecast, made in early May, is substantially higher than the one made last October. At that time, prior to the drop in crude oil prices, the panel expected demand of 6.813 million b/d in 1986. The price drop is the main factor in IPAA's increased demand expectations.

Motor gasoline demand peaked in 1978 at 7.412 million b/d. It plummeted to 6.539 million b/d in 1982 in the wake of the 1979-80 oil price jump.

Since then demand has moved up slowly, reacting mainly to economic activity and price drops. Motor gasoline demand increased 1.3% in 1983 to 6.622 million b/d. It moved up 1.1% in 1984 and 1.8% in 1985.

**The stocks picture.** Primary gasoline stocks increased during the winter as refiners produced distillate for the heating oil market.

Total primary motor gasoline stocks, including blending components, moved up to 244.8 million bbl at the end of February.

However, from early March through April total motor gasoline stocks dipped to 209.1 million bbl. There has been a slight increase since then. For the week ending May 30, the level was 218.8 million bbl.

The days of supply represented by motor gasoline stocks fell from 38.08 days at the end of February to 29 days in April and 32.2 days in May.

Most of the primary stocks are needed to keep the distribution network operating.

The May 30 stock level was only 18.8 million bbl more than what the Energy Information Administration considers the minimum operating level for gasoline, based on a National Petroleum Council committee report in November 1983 (NPC). That's less than 3 days' supply.

However, since November 1983 numerous refineries have closed, and crude oil prices have collapsed.

One member of the NPC committee that estimated minimum operating levels says 160 million bbl may be a better figure for gasoline at present. At current demand, the difference between that and the May 30 stock level represents 8.6 days of supply.

Crude stocks rose to 345.3 million bbl at the end of March from the yearend 1985 level of 318.7 million bbl. At the end of May crude stocks were 324.7 million bbl.

Refinery utilization rates are improving. The rate was 86.7% for the week of May 30. API says industry's present operable capacity is 15.511 million b/d, and the input to crude oil distillation units for the week of May 30 averaged 13.455 million b/d.

**Secondary storage.** A major reason stocks fell rapidly from early March through April was that gasoline was moving from primary to secondary storage, says Edward N. Krapels of Energy Security Analysis Inc., Washington, D.C. He estimates the total volume of such transfers in the U.S. and Europe at 500,000 b/d.

U.S. secondary storage for gasoline has been estimated by NPC at 106 million bbl. In addition, as much as an additional 20 million bbl of distillate storage capacity can be used for gasoline, Krapels says.

"Given a secondary gasoline storage capacity of as much as 130 million bbl, a 28 million bbl transfer from primary to secondary seems well within the bounds of reason.

"Moreover, when this transfer began in early March, U.S. spot prices and near term futures prices for gasoline were 37¢/gal, while retail prices were still about 90¢/gal.

"As mesmerized as many of us are by the futures market, the majority of operators in the secondary sector do not take major positions at the New York Mercantile Exchange.

"Thus, when the spreads between retail and rack prices indicate a seemingly sure-fire opportunity to turn a hefty inventory profit, especially when that opportunity comes at the end of the heating season, one can expect a significant shift in inventories from the primary to the secondary sector."

Refiners, aware that the changes in primary stocks indicated something besides more consumption, didn't rush to boost their own gasoline stocks.

"Those (secondary) inventories aren't tracked as religiously as primary storage, so there's just not as good information on what is going on there," says one Texas refiner.

SELF
SERVE
STANDARD OIL
On The Way

**Revamped service station** is one example of how Standard Oil Co. and affiliates seek to boost their U.S. gasoline market share, estimated by Lundberg Survey Inc. at 3.6% as of February 1986. Photo courtesy Paul Fusco/Magnum Photos.

"When prices start to jump, the jobbers all tend to fill their tanks, which pulls the primary down quicker than the secondary. But that's really not a true indication of more demand."

**Imports steady.** Imports are not shaping up to be an unusually large portion of this summer's motor gasoline supply. As a percentage of U.S. demand, imports of gasoline and components are declining from the high levels of 1984 and early 1985 to historic levels. From 1982 through early 1985 imports rose steadily and reduced the U.S. refinery utilization rate by several percentage points (OGJ, Mar. 4, 1985, p. 50).

During March-May 1985, imports of gasoline and components rose to an average 552,786 b/d—8.1% of U.S. gasoline demand.

That contrasts with 1973-82, when the share of U.S. gasoline demand filled by imports of gasoline and components ranged from 1.9% to 3.1% and averaged 2.5%. During June-December 1985, imports fell to 420,429 b/d—6.9% of demand. For the first 5 months of 1986 gasoline imports have averaged 350,000 b/d or about 5.1% of present demand.

**Why supplies increased.** In retrospect, the increase in gasoline and component imports that threatened or appeared to threaten small refiners had little to do with predatory pricing by exporters or new processing capacity among members of the Organization of Petroleum Exporting Countries, says Dr. Fereidun Fesharaki, leader the Energy Program at the East-West Center, Honolulu.

The most widely discussed reason was a British coal strike that resulted in an additional 500,000 b/d in demand for fuel oil.

To meet that extra demand refiners increased runs, leaving the market with surplus light product.

"Coupled with a buoyant U.S. economy and depressed demand elsewhere, there is little wonder that U.S. light product imports swelled," he says. Another reason for the recent worldwide surplus in light products has to do with the cracking/crude run ratio. "The ratio of cracking capacity to distillation rose rapidly from the late 1970s onward," Fesharaki says. "As crude runs fell, however, the ratio of cracking to crude runs rose explosively. Worldwide, the ratio rose from about 21% in 1978 to about 34% in 1984.

"In the U.S. the ratio rose from about 55% to nearly 80% in the same period. Worldwide, the amount of cracking was in excess of the amount of fuel oil that required upgrading."

The result was a general surplus of light products, a shortage of fuel oil for upgrading, and a narrowing of margins between light and heavy crudes to a degree that would once have been deemed impossible.

**Prices firm.** EIA estimates that summer gasoline prices may drop as much as 28¢/gal below last summer's levels and should be about equal to prices during the summer of 1979.

The pump price of motor gasoline started falling sharply in early December 1985, along with crude oil prices.

According to the OGJ survey, the average pump price of leaded gasoline fell from $1.171/gal in December 1985 to $0.9114/gal in April 1986. This was a drop of 25.96¢/gal or 22.2% during the period.

## Increase seen in average U.S. driving

Average driving by the U.S. automobile fleet is expected to increase this year to about 10,200 miles/vehicle from last year's estimated 9,990 miles.

The average miles driven per car peaked at 10,184 miles/year in 1972.

It dropped sharply to 9,448 miles in 1974. In 1978 it climbed to 10,046 miles. By 1981 driving had fallen to 9,002 miles/year/car with the surge in gasoline prices and an economic slowdown.

As ~~prices~~ slowly declined and economic conditions improved, average miles driven rose to 9,809/car in 1984.

Prior to the first oil price shock in 1973, the efficiency of the U.S. auto fleet in terms of miles driven per gallon of fuel consumed was declining. It dropped from 13.93 mpg in 1967 to a low of 13.1 mpg in 1973. After the price hikes of 1973-74 and 1979-80, consumer demand for more fuel-efficient vehicles and government-mandated fleet fuel efficiency rules led to more efficiency. Annual fuel efficiency ratings have consistently improved, with the average increasing to 16.94 mpg in 1984 and an estimated 17.6 mpg 1985. The size of the gasoline vehicle fleet has climbed steadily with the population and economic growth. The fleet has increased from 154.4 million vehicles in 1981 to 166.6 million in 1985.

Motor gasoline consumption also has been boosted by the aging of the car fleet. The average age of cars in the U.S. has moved up to 7.5 years in 1984 from a low of 5.5 years in 1969. The increase in average age means slower replacement of the older, less fuel efficient vehicles.

The average pump price of self-service unleaded gasoline fell from $1.1729¢/gal to $0.9023/gal.

This sharp drop in motor gasoline prices has helped boost demand.

The increase in consumption and the expectations of increased demand throughout the driving season have prompted gasoline marketers to try to increase margins. And the consequence has been a slight increase in gasoline prices in recent weeks.

During the last 6 weeks the pump price of unleaded motor gasoline has moved back up to 94.76¢/gal on June 6, an increase of 4.53¢/gal.

**Ethanol stumbles.** The economics of ethanol production and blending fell with this year's historic crude oil price collapse.

As a result, many refiners dropped ethanol. Amoco Oil Co. dropped ethanol in unleaded products in Iowa, Nebraska, and Southeast South Dakota. Mobil Oil Corp. ended its ethanol blending and marketing experiment in Minnesota and Illinois. Total Petroleum Co. eliminated ethanol from all its branded regular leaded and unleaded gasoline grades. Unocal Corp. dropped ethanol from its Florida gasolines. U.S. fuel ethanol blend sales totaled 2,004,833,000 gal during first quarter 1986, says IRI. That's up from 1,803,288,000 gal in the same period in 1985, but down 15% from fourth quarter 1985.

Early last month the Agriculture Department moved to cut ethanol's production costs. The department said it would allow ethanol producers to earn commodity certificates issued by the Commodity Credit Corp. (CCC) if they demonstrate that grain was removed from the market and processed into ethanol by Sept. 30, 1986.

IRI Pres. Frederick L. Potter says ethanol profit margins will improve over what had been expected, due mainly to the CCC program. The turnaround began 2 months ago. Sales of ethanol for May are projected at 69.5 million gal, up from the 1986 low of 59.7 million gal in February.

**Marketing scramble.** Gasoline marketing this summer is costly and fierce. Two developments, in particular, are forcing refiners and marketers to pay more attention to product specifications and advertising. The first is the rising demand for premium unleaded and the midgrade unleaded and the falling demand for leaded regular.

EIA says that all unleaded gasolines were up to 67.5% of total product supplied for the U.S. in March 1986.

One major refiner said that regular leaded accounts for 20-25% of his total gasoline sales and premium unleaded, 27-28%. That compares with last summer when his regular leaded sales were at 30% or more of the total pool and the premium unleaded was about 22%, he says.

"So the big swing has been in premium unleaded vs. regular leaded."

Refiners with sufficient octane capacity are boosting their efforts to capture as much of the rising premium unleaded market share as possible.

Two smaller Texas refiners say that if the midgrade unleaded claims a larger market share than regular unleaded, they and others like them will be hurt. Some refiners are testing markets to see if they should drop leaded regular. About 2 months ago Mobil began an all unleaded program in Manhattan after sales of regular leaded fell to less than 10% of dealers' sales.

The second development concerns ethanol, which has been hit by a "negative advertising campaign," says IRI's Potter. "If independents are denied their alternative and most cost effective source of octane, ethanol, then premium unleaded market share for the major oil companies will increase."

**Opportunities.** During the summers of 1986 and 1987, refiners with idle or shutdown conversion capacity that can be brought on stream for the driving season may enjoy strong margins, says Robert E. Cunningham of Turner, Mason & Co., Dallas consulting engineers.

"Historic industry trends plus developments that appear to be unique to 1986 and 1987 are converging to boost the economics of gasoline production," Cunningham says.

The historic trends include extra demand from increased vacation driving, decreased supply from the seasonal need to reduce gasoline volatility, and the lead phasedown program.

Refiners in the next two summers, he says, will not have full use of the new octane upgrading units that are being designed and built in response to the lead phasedown.

"Until those units come on stream, U.S. gasoline supply, especially unleaded premium, will be tight."

But a tighter market is more likely to result from higher demand.

"We saw indications of a tight gasoline supply on the West Coast last summer," says Cunningham.

"At that time it became evident that gasoline production capacity on the West Coast was full, and demand for motor gasoline was still increasing. That excess demand was met by more shipments of gasoline from the Gulf Coast. Of course, if the entire industry rushes out and restarts all their shutdown conversion capacity without subjecting such projects to rigorous economic tests, the opportunity for a continuation of the current strong refining margins will be lost." ▪

TOYOTA
TOYOTA

**Polyethylene** is stored prior to export at this Saudi Basic Industries warehouse in Sharq. It's part of the company's growing global distribution center.

# Middle East petrochemicals flow to western Europe despite tariffs

**Roger Vielvoye,** International Editor
**Michael Obel,** Staff Writer

Petrochemicals from new plants in the Middle East are flowing into western Europe despite European Community (EC) tariffs on several key products.

Since the beginning of this year the community has slapped tariffs ranging from 12.5% to 13% on petrochemicals from plants operated by Saudi Basic Industries Corp. (Sabic) and several foreign partners in Saudi Arabia.

In the first 5 months of the year, strong demand for commodity chemicals and plastics allowed Middle East imports to find a niche in the European market without causing big problems for producers in the region.

European petrochemical producers got a boost from that strong demand, falling feedstock prices, and a series of technical problems at major plants that reduced supply.

Last summer, for example, Enichem SpA's Priolo, Sicily, ethylene plant experienced fire damage that was not fully repaired until April of this year. Enichem used ethylene imported from Saudi Arabia to supplement its supply.

If the petrochemical market falters, domestic plants will start to feel the full effect of rising Saudi shipments to Europe.

Some of the problems caused by Saudi imports crop up because all the shipments are handled by companies not based in Europe.

In the late 1970s and early 1980s, when Sabic was looking for joint venture partners, European petrochemical producers ignored the opportunities, leaving the partnership field exclusively to U.S. and Japanese companies.

That may be changing, however.

Italy's Enichem and Neste Oy of Finland recently took an interest in a 500,000 ton/year methyl tertiary butyl ether plant in partnership with Sabic, which holds a 70% interest in the venture.

More than 70% of Saudi Arabia's petrochemical sales enter the export market. That spells a rising level of profits for Sabic: $40 million in 1985, 4.2 times its 1984 profit and 7.3 times its 1983 profit.

The EC complains that in less than 1 year the Saudis have captured the top spot in every petrochemical they sell.

The community rejects Saudi charges that EC tariffs amount to protectionism.

In the global context, western Europe is one of the most competitive areas for petrochemicals. Local manufacturers compete with imports from eastern Europe, Canada, the Middle East, and North Africa.

EC claims that Saudi imports are treated more favorably in Europe than in the U.S. or Japan. The U.S. offers no duty-free concessions—even to its Canadian and Mexican neighbors—with the result that Canadian products are exported to Europe. And eastern European petrochemicals face a 45% duty when they are sold into the U.S.

So when new plants start up, operators look to the most profitable markets and, therefore, turn to Europe.

**The cause.** New Saudi petrochemical plants began exports in earnest in 1985 amid forecasts of doom from many European commodity chemical manufacturers. They feared that increased supply of products would undermine the continent's oversized polyethylene capacity.

As Saudi imports mounted, EC stepped in with its first round of duties in August 1985. Toward the end of the following November an agreement was reached with the Saudis that increased the volumes of Saudi products that could enter Europe duty-free.

That, combined with talks at the Gulf Cooperation Council (GCC) level aimed at starting negotiations over a broad trade agreement, led to expectations by Arab producers that EC would take a more relaxed view of imports in 1986.

Against this background, swift action by EC early last January came as a shock to Sabic and its joint venture partners.

By Jan. 6, imports of linear low density polyethylene (Lldpe) were three times the annual duty-free allowance and were slapped with a 12.5% tariff.

Only 3 days later a similar tariff on high density polyethylene (HDPE) went into force. And on Jan. 13 a 13% tariff on methanol was introduced.

Since then duties have been placed on Saudi diethylene glycol, ethylene glycol, styrene, melamine, and urea.

All the quotas are defined in European Units of Account, which carry their French acronym ECU.

The ceiling on diethylene glycol was 340,300 ECU, worth about $225,000. At the time the duties were imposed the quota on diethylene glycol had been exceeded almost 10-fold.

European sources say the quotas are low compared with the volume of imports. The 3.3 million ECU ceiling on methanol is equivalent to a single import cargo from Saudi Arabia.

Europeans also say that even in 1985, when Saudi production was just starting to build, Sabic and its partners exceeded their quotas of polyethylene 16-fold.

In 1986 the Saudis have an even greater capacity to export into Europe. Of Sabic's 12 first generation plants, only two—Petrokemya and Sharq—are not fully on stream. Those plants are in start-up.

**The effect.** According to the EC and the European Council of Chemical Manufacturers' Federations, which monitor the situation, the underlying problem is that Europe continues to attract a disproportionate share of production from new Saudi plants.

This is a problem that has concerned Europeans since the late 1970s, when the Saudis began planning their entry into the petrochemical industry business, mainly in partnership with U.S. and Japanese companies.

The European petrochemical market was suffering from massive surplus manufacturing capacity, particularly in ethylene products, where the Saudis are strongest.

European manufacturers feared the outcome would be enforced plant closures, with some domestic producers possibly going out of business.

The threat of a flood of cheap products from the Middle East provided the impetus for a much-needed rationalization program.

A number of large plants have closed in the last few years. Most companies now employ a strategy of playing to their strength. With this in mind they are disposing of capacity in areas where they cannot become competitive, top players.

Unwanted capacity is normally sold to companies that have made long term decisions to remain in this sector of the market.

But, as one executive explained, the current revivals in demand and prices could temporarily check some parts of the rationalization, although it needs to continue.

**Some examples.** Earlier this year Imperial Chemical Industries plc (ICI) and Enichem agreed to merge their unprofitable polyvinyl chloride (PVC) interests into a joint venture called European Vinyls Corp.

After shutting down 300,000 tons/year of unwanted capacity the new unit will still have 2.2 million tons/year of capacity, making it the largest manufacturer in Europe with about 25% of the market.

ICI is waiting for final approval from the EC on the Enichem deal. After its first 2 years, the deal should have removed about half the PVC overcapacity in Europe.

The other major rationalization undertaken by ICI was in low density polyethylene (LDPE), where it started to back out of the market once it saw the extent of the Saudi import threat.

In a deal with Atochem of France, part of Ste. Nationale Elf Aquitaine, it disposed of much of its LDPE business and, at the same time, took on the French company's ethylene oxide derivative business.

Recently, it sold its 100,000 ton/year operation at Fos in southern France to the Royal Dutch/Shell Group, which also is rearranging its petrochemicals operations.

Shell Nederlands has acquired Hoechst Nederlands' polystrene operations. This will give Shell 80,000 tons/year of general-purpose and toughened polystrene and 70,000 tons/year of expandable polystyrene, its first access to these markets.

Atochem's rationalization program included a deal with BP Chemicals Ltd. to merge polypropylene interests into a joint venture. Capacity at the Atochem plant at Gonfreville near Le Havre and at BP's Lavera plant will be increased. Outdated capacity will also be closed.

BP also is expected to announce shortly that it will take over marketing all polyethylene output from the joint BP/Bayer plant at Dormagen in West Germany.

All production is now marketed by Bayer, which has no other interest in polyethylene. The agreement would reduce the number of companies marketing polyethylene and give BP access to almost 900,000 tons/year of capacity, behind the market leader, Enichem.

BP has developed a new production technology at Lavera and is consider-

**Petrochemical plant,** BP Chemicals Ltd.'s Grangemouth facility on the Firth of Forth in Scotland, is one of the company's largest processing facilities. It has a 240,000 ton/year ethylene cracker and major polyethylene production facilities.

ing using it to replace older polyethylene plants at Dormager or Grangemouth, Scotland. At Dormager, BP is negotiating a takeover of the subsidiary's joint production.

**Partners react.** Despite the EC tariffs, Sabic's foreign partners do not report many problems selling their goods in Europe or finding appropriate ways to trim their non-Sabic capacity.

Essochem Europe Inc., the European affiliate of Exxon Chemical Co., said the EC tariffs have not affected its plans for importing product from the parent company's Kemya joint venture with Sabic.

"The tariffs have not restrained imports from Saudi Arabia," said a spokesman. "They have merely made the products more expensive for our customers."

Essochem will not comment on the amount of Saudi products being imported into Europe to supplement the output of its two manufacturing plants in Belgium.

The units at Meerhour and Zwijndrecht near Antwerp have a combined capacity for high and low density polyethylene of 560,000 tons/year. The units receive feedstock from Essochem's share of the Mossmoran ethylene cracker in Scotland.

Before the Sabic/Exxon Kemya plant began exporting, Essochem began cutting its European capacity.

The 450,000 ton/year ethylene cracker at Cologne in West Germany was shut down. The 365,0000 ton/year ethylene cracker and associated plants at Stenungsund, Sweden, were sold to Norway's state-owned Den norske stats oljeselskap AS.

Esso says introduction of imports from Saudi Arabia has made no difference to production at the two Belgian plants. Neither produced Lldpe, which makes up the bulk of the imports from Saudi Arabia.

Imports from Saudi Arabia started in the second half of last year, and Essochem has been forced to live with the import tariffs for most of this time.

Mobil Corp. established a company, Mobil Polymers International, in Brussels to sell in 28 countries its share of production from the new Saudi Yanbu Petrochemical Co. (Yanpet) plant on Saudi Arabia's Red Sea Coast.

Sales work began before the plant began operating and resulted in a network of customers by the time the plant came on stream.

For the 12 months ending Apr. 1 Mobil reported that "strong worldwide sales" kept the Yanbu plant running at more than design capacity for all three of its products. The facility is rated at 450,000 tons/year of ethylene, 320,000 tons/year of polyethylene, and 200,000 tons/year of ethylene glycol.

Mobil says recent strong sales reflect "improved industrial activity, especially in the Far East, and early customer acceptance of the new plant's diversified line of plastic resins.

"For all our sales efforts, we wouldn't have met customer demand were it not for Yanpet's trouble-free start-up period and its ability to maintain production of prime grade petrochemical resins at design-plus capacity," says Arthur E. Biggs, Mobil Chemical Co. president.

**EC/GCC meeting.** Meanwhile the EC hopes late this year to sign a broad cooperation agreement with the GCC, which represents all the Arab countries around the Persian Gulf except Iraq.

A series of exploratory talks between the two sides ended in Riyadh last month, and the EC is formulating proposals to be put to the European Council of Ministers later this month.

Provided there are no last minute objections from individual countries, negotiations on a wide-ranging trade, research, and training agreement could start in the fall.

The question of petrochemical imports will be included in the talks on trade.

It is possible a new EC/GCC trading pact would give all the petrochemical producers in the Gulf greater access to European markets, replacing the existing generalized system of perferences (GSP) volumes and duties.

The tariffs that have upset the Saudis were imposed as part of the GSP that allows developing countries limited, duty-free access to European markets.

The system was introduced in the late 1960s. At that time, no one expected a developing country like Saudi Arabia to plow billions of dollars into becoming a force in the world petrochemicals market in less than a decade.

Under GSP, the volume of imports in relation to total Saudi petrochemical production is very low.

**Sabic's view.** Sabic says its marketing is primarily driven by where it can make the most profit.

"Sabic's petrochemical products are marketed worldwide," says Ibrahim A. Salamah, Sabic's managing director.

But the company also says it is moving carefully, not opportunistically.

Sabic's director general of planning and research, Nasser A. Sayyari, says the company will market its production in a steady, measured fashion.

"Neither Sabic nor its foreign partners ever entertain the thought of dumping products," says Sayyari.

"We persistently endeavor not to let a surplus Saudi product finish up on the spot market. If the potential buyer of Sabic product usually takes a substantial portion or all of the output of a competitor's plant, Sabic will have no time for him."

European concerns about Saudi domination of the continent's petrochemical market may be further allayed by Sabic's interest in non-European markets.

"The greater Indian Ocean areas have enormous long term potential as a market for petrochemical products, including polyethylene."

He also says a "considerable portion" of Sabic sales last year were directed to Asian and African countries. ▪

# Surplus capacity still plagues W. European refiners

The refining industry in the 12 member European Community (EC) has too much primary distillation capacity despite a series of plant shutdowns.

EC capacity fell by 810,000 b/d to 12.64 million b/d during 1985. Taking into account this reduction, the European Commission says, there is still 1 million b/d of excess capacity, based on an average utilization rate of 80%. Further closures planned mainly in France and Italy, are scheduled to reduce EC primary distillation capacity to 11.78 million b/d by 1990.

Utilization rates for primary distillation capacity varied considerably last year. In West Germany, Britain, and Denmark, rates were more than 80%. But Italy and Portugal reported less than 60%. Utilization rates for conversion capacity were generally higher, averaging about 82%.

**Prices, imports.** The European Commission, which bases its report on interviews with refiners, governments, and trade unions, says it is difficult to assess future relationship between capacity and demand because of uncertainties about crude prices. So the commission produced three price scenarios.

The base case involves $20/bbl oil for the rest of the decade, which would leave EC oil consumption at its present level to 1990.

If the price leveled out at $15/bbl, demand would increase by about 10% during the period. And if the price recovered to $25/bbl, there would be a 5% drop in demand.

## The shrinkage in EC primary distillation capacity*

| | Maximum capacity† | 1980 | 1985 | 1986 | §1990 |
|---|---|---|---|---|---|
| | | | Million b/d | | |
| Belgium | 1.13 | 1.13 | 0.63 | 0.63 | 0.61 |
| Denmark | 0.25 | 0.25 | 0.16 | 0.16 | 0.16 |
| France | 3.59 | 3.43 | 2.28 | 2.28 | 1.99 |
| West Germany | 3.26 | 3.16 | 2.13 | 1.80 | 1.62 |
| Greece | 0.41 | 0.41 | 0.36 | 0.36 | 0.36 |
| Ireland | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 |
| Italy | 0.76 | 3.69 | 2.63 | 2.50 | 2.30 |
| Netherlands | 2.09 | 2.09 | 1.52 | 1.50 | 1.37 |
| Portugal | 0.39 | 0.39 | 0.28 | 0.28 | 0.28 |
| Spain | 1.47 | 1.47 | 1.37 | 1.27 | 1.27 |
| U.K. | 2.84 | 2.81 | 2.03 | 1.80 | 1.76 |
| **Total** | **19.25** | **18.89** | **13.45** | **12.64** | **11.78** |

*Capacity as of Jan. 1 each year. The 12th EC member, Luxembourg, has no refineries. †Maximum capacity reached in 1980 by Spain and Portugal, 1979 by West Germany, 1978 by U.K., and 1977 by others. §Estimate based on published closure notices and information from oil companies.

Source: European Commission

Working out the level of primary distillation capacity needed by EC members by 1990s is complicated by products imports.

The commission has not changed its view, put forward last year, that new export refineries in the Middle East and North Africa will place an added 1 million b/d of products on the market by 1990. It noted, however, that key domestic refinery projects in Saudi Arabia have been canceled. So some products from export refineries are being diverted to internal use.

Excluding feedstocks, EC's net products imports of 616,000 b/d in 1985 were 103,000 b/d higher than forecast. Uncertainty also surrounds the future level of imports.

EC's net imports, excluding feedstocks, might increase from the 1985 level to 822,000 b/d by 1990. That is based on the assumption that more imports from the Middle East and North Africa will move into EC countries in accordance with market forces and without government intervention.

**Capacity shutdowns.** Commission data show that in the $20/bbl base case closure of 1.3 million b/d of EC primary distillation capacity will be needed, including 860,000 b/d currently planned, to reach a satisfactory utilization rate.

Oil at $15/bbl will not require a major reduction in capacity beyond the planned 860,000 b/d. Primary distillation capacity and demand will be broadly in balance, although one or two obsolete refineries might have to be shut down. A stabilized price of $25/bbl will require closures totaling 1.95 million b/d, continue the contraction of the fuel oil market, and require more spending for deep conversion units after 1990. Even in the scenario of highest consumption there will be enough spare capacity in EC member country refineries to meet community demand. However, there might be a need for increased imports of some products. None of the scenarios presents security of supply problems, the European Commission said. ▪

# Shortage predicted for U.S. ethylene supply

Lower crude oil prices will cause a shortfall in U.S. ethylene supply and capacity in the early 1990s.

So the U.S. petrochemical industry should add at least 6 billion lb/year of ethylene capacity during 1990-95 to meet expected 1995 demand, says Chem Systems Inc. (CSI), Tarrytown, N.Y.

But uncertainty over energy prices and markets, along with potential competition from imports and other products, will leave the U.S. industry loath to add ethylene capacity this century.

**Ethylene supplies tighten.** Total active U.S. ethylene capacity is about 34 billion lb/year, CSI estimates.

Because the U.S. industry shut down 6 billion lb/year of ethylene capacity during 1982-83, its effective utilization rate jumped to as much as 98-99% in 1984-85 from about 78-81% in 1980-81.

CSI estimates, however, that U.S. ethylene demand will reach 35.7 billion lb/year by 1990 and 40.6 billion lb/year by 1995. That works out to an average growth of 2.5%/year during 1985-95, just lagging predicted gross national product growth of the same period.

Several factors will delay the U.S. ethylene shortfall until the 1990s.

For example, some ethylene capacity temporarily shut down in 1982-83 went back on stream by 1985. And the newer heavy liquids crackers built during the late 1970s never have run at maximum conditions and perhaps could operate at 10-15% more than nameplate capacity.

Running the heavy liquids crackers at higher rates and some further debottlenecking may add as much as 3 billion lb/year of U.S. ethylene capacity this decade, CSI estimates.

**Foreign competition.** Meanwhile, the full extent of the threat of ethylene imports to the U.S. has not materialized, CSI says.

Early expectations were that incremental world ethylene demand would be met by burgeoning exports from resource-rich nations such as Canada and Saudi Arabia. But with the first wave of ethylene export projects completed, CSI sees little threat of a second wave.

The expected slowdown of added olefins export development stems from a lack of capital, prolongation of the early 1980s recession, and export projects' loss of competitive edge due to lower oil prices.

If crude prices don't rebound long term, don't expect the second wave of big export projects to be built, says CSI.

**The outlook.** CSI expects only minor increments of export olefins capacity to be added selectively and carefully during 1990-95 as product from the first wave of projects enters the world market.

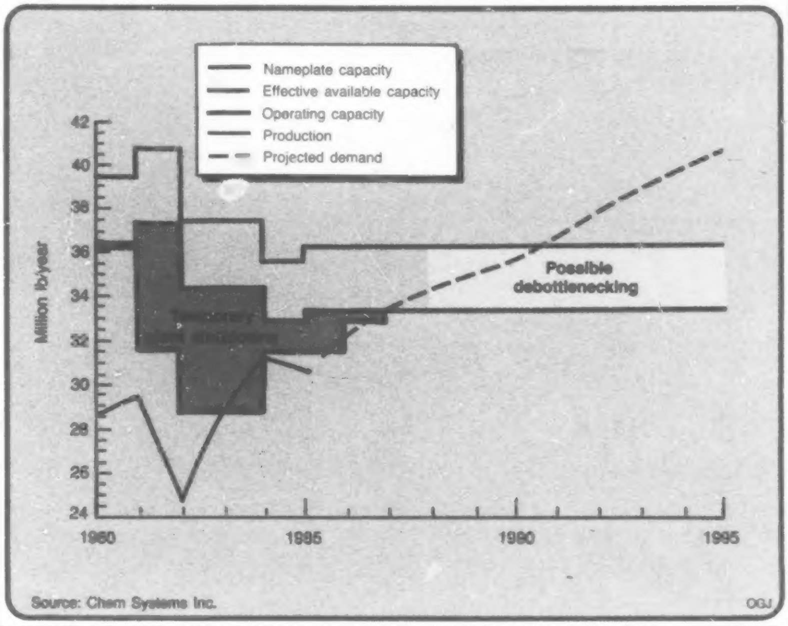
That's because lenders burned by bad energy project loans due to the oil price collapse will be very careful about financing any new projects.

Moreover, multinational oil companies assessing world feedstock supply sources will have to weigh the economics of ethylene imports against increasing volumes of U.S. naphthas and butanes that will be backed out of the gasoline pool and forced elsewhere, likely at very competitive prices.

"Considering the recent poor performance and bloodletting that the U.S. ethylene industry has undergone because of its overoptimism in projecting the need for, and building, excess capacity in the mid to late 1970s, it is understandable why many in the industry predict that there will be no new ethylene capacity built in the U.S. during the remainder of this century," CSI said.

"It is easy—and a common error—for a longer term forecast to be misdirected by short term conventional wisdom." ▪

The shortfall in U.S. ethylene supply



Source: Chem Systems Inc.

OGJ

# Conoco will reduce U.S. refinery runs

A growing U.S. inventory of petroleum products has caused Conoco Inc. to reduce crude runs.

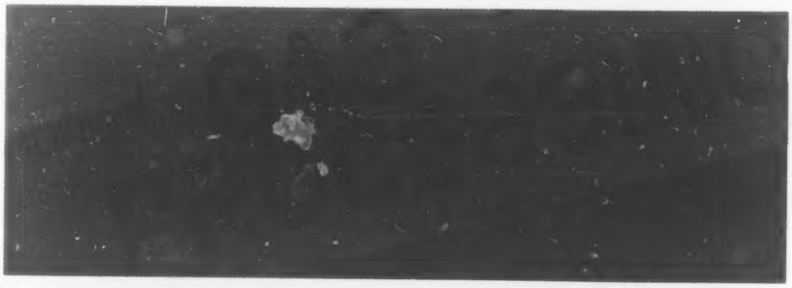
Conoco last week disclosed it is reducing runs by nearly 50,000 b/d at its Lake Charles, La., and Ponca City, Okla., refineries.

Lake Charles processing will be reduced by 28,000 b/d, or 17%. Ponca City will be cut 20,000 b/d, or 15%.

Conoco refineries at Billings, Mont., Santa Maria, Calif., and Denver will maintain current levels of production.

The company's refineries have been running at close to 94-96% utilization. The reductions will cut utilization rate to about 80% at Lake Charles and Ponca City.

"It is apparent that the refining segment of the industry has been operating at a rate in excess of customer demand," said Gary Edwards, Conoco vice-president for North American refining, marketing, and transportation.



**Canadian gas-processing plants** typically produce elemental sulfur, as the mounds at Canadian Occidental's Petrogas plant near Calgary show, along with NGL. The Petrogas plant can process 210 MMcfd of gas and produce some 800 ton/day of sulfur.

# Gas-processing pace livelier outside U.S.

## About this report . . .

Extraction of valuable components from natural gas and its cleanup is still a lively enterprise worldwide, as shown in two exclusive, major OGJ surveys in this special report — Worldwide gas processing (p. 60) and Petroleum-derived sulfur (p. 90), and in an update on the current U.S. LPgas business.

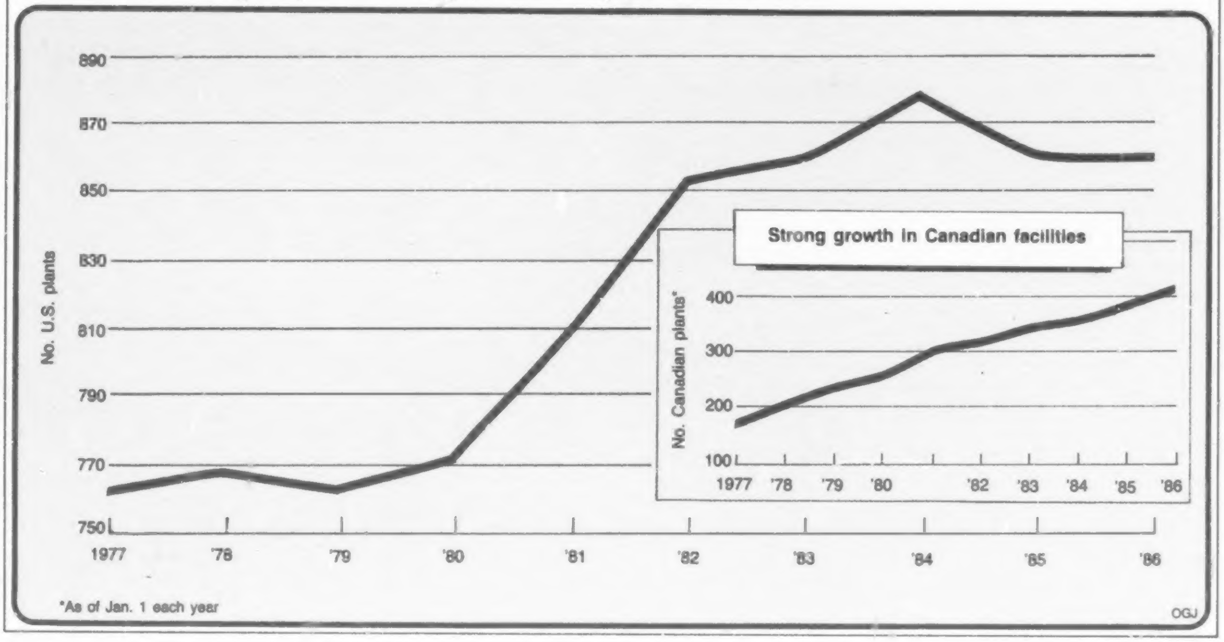
**Leo R. Aalund**
Technology Editor

In terms of natural gas throughput and output of NGL, the U.S. gas-processing industry has been drifting while Canada and the rest of the world were moving at a quicker pace in 1985.

This development is reflected in the Journal's most recent plant-by-plant, worldwide gas-pro-

Fig. 1

## Rise in U.S. gas processing plants dips and flattens



*As of Jan. 1 each year

cessing survey, which is a part of this special report along with OGJ's exclusive international survey of petroleum-derived sulfur recovery. The latter shows a continuing gain in this type capacity.

Canada and the U.S. dominate the world totals with their gas-processing capacity, throughput, product output, and sulfur-recovery capacity and production.

Almost 90% of the world's gas-processing plants are found in the U.S. and Canada, as Fig. 1 indicates, and over 60% of the capacity is in those two countries. The U.S. accounts for 48% of the gas-processing capacity, Canada for 16%. Canada leads the world in sulfur recovery capacity with 28,400 metric ton/day, according to the Journal's sulfur survey which begins on p. 90. It is followed by the U.S. with 26,000 metric ton/day. The rest of the world has 34,000 metric ton/day capacity. The U.S., however, has more sulfur recovery facilities with 148 vs. 50 in Canada, leaving 172 in all other countries.

There are a far greater number of facilities outside even Canada, though it has the largest total capacity, because they are mostly associated with refinery operations, which require smaller sized units. Most of the Canadian units, on the other hand, process large flows of natural gas that frequently have exceptionally high contents of hydrogen sulfide.

If the sulfur recovery plant is in a location with strict environmental regulations it can be the most important unit in a refining or natural gas-processing complex. If it goes down or is not performing adequately, the rest of the complex may have to be shut down.

Table 1

## Gas processing activity in various regions

| | 1984 | 1985 | Change | Change, % |
|---|---|---|---|---|
| **U.S.** | | | | |
| Gas throughput, MMcfd | 40,474.2 | 38,753.8 | −1,720.4 | −4.4 |
| Gas liquids production, 1,000 gal/day | 60,094.3 | 56,378.1 | −3,716.2 | −6.6 |
| Proven gas reserves, billion cu ft | 198,000.0* | 197,000.0† | −1,000.0 | −0.5 |
| **Canada** | | | | |
| Gas throughput, MMcfd | 11,921.0 | 12,447.8 | +526.8 | +4.2 |
| Gas liquids production, 1,000 gal/day | 15,133.4 | 17,381.7 | +2,248.3 | +12.9 |
| Proven gas reserves, billion cu ft | 92,300.0* | 99,700.0† | +7,400.0 | +7.4 |
| **Rest of the world§** | | | | |
| Gas throughput, MMcfd | 29,942.3 | 31,083.3 | +1,141.0 | +3.7 |
| Gas liquids production, 1,000 gal/day | 49,529.2 | 52,152.6 | +2,623.4 | +5.0 |
| Proven gas reserves, billion cu ft | 1,614,325.0* | 1,641,360.0† | +27,035.0 | +1.6 |

*As of Jan. 1, 1985
†As of Jan. 1, 1986 §Excludes Communist bloc and China

However, in terms of investment, the gas-processing plants are the most important. Here is an area-by-area analysis on how this industry was structured and operated as of the first of this year.

**U.S.** As a result of processing 38,753 MMcfd of natural gas in 1985, the U.S. gas-processing industry turned out 56.4 million gal/day (some 1.34 million b/d) of total products which run the spectrum from ethane through propane, butanes, mixes, and debutanized natural gasoline. As Fig. 2 shows, the U.S. is no longer the major producer of NGL. It accounted for over 50% of non-Communist world output in 1980 compared to 43% last year. There are many reasons why NGL output falls, but a first principle is that if the natural gas isn't processed the liquids won't be produced. U.S. natural gas production has been declining since 1979 except for a minor revival in late 1984 (Fig. 3 and Table 1). Production may test new lows this year as the price of crude oil hangs in at low levels.

Table 2

## Major U.S. gas-processing states in 1985

| | Gas throughput, MMcfd | Share of total throughput, % | Gas capacity, MMcfd | No. of plants | NGL production, 1,000 gal/day | Share of total NGL product, % |
|---|---|---|---|---|---|---|
| Texas | 12,116.4 | 31.3 | 19.630.8 | 384 | 26,548.6 | 47.1 |
| Louisiana | 10,758.5 | 27.8 | 20,366.4 | 94 | 10,085.2 | 17.9 |
| Kansas | 3,418.0 | 8.8 | 5,646.0 | 28 | 2,280.8 | 4.0 |
| Oklahoma | 2,898.2 | 7.5 | 4,989.8 | 108 | 5,692.2 | 10.1 |
| New Mexico | 1,924.1 | 5.0 | 3,141.6 | 34 | 3,461.7 | 6.1 |
| Michigan | 1,589.3 | 4.1 | 4,734.9 | 26 | 963.8 | 1.7 |
| Wyoming | 1,188.9 | 3.1 | 1,897.9 | 41 | 1,627.7 | 2.9 |
| Arkansas | 870.4 | 2.2 | 962.5 | 6 | 104.6 | 0.2 |
| California | 731.8 | 1.9 | 1,066.0 | 36 | 1,340.3 | 2.4 |
| Florida | 678.8 | 1.8 | 799.0 | 3 | 454.8 | 0.8 |
| **Subtotal** | **36,174.4** | **93.5** | **63,234.9** | **760** | **52,559.7** | **93.2** |
| **Other states** | **2,579.4** | **6.5** | **4,494.2** | **102** | **3,820.4** | **6.8** |
| **Total** | **38,753.8** | | **67,729.1** | **862** | **56,378.1** | |

Table 3

## Worldwide gas processing-plant construction*

| Area | 1985 | 1986 |
|---|---|---|
| United States | 31 | 28 |
| Canada | 15 | 6 |
| Latin America | 5 | 5 |
| Europe | 5 | 8 |
| Middle East/ Africa | 8 | 5 |
| Asia-Pacific | 9 | 8 |
| Total | 73 | 60 |

*Planned, expanding or under construction

Gas processors are strongly affected, rather buffeted now, by the differential in price for thermal units from crude oil vs. those from natural gas. The precipitous fall in crude oil prices early this year still has to work its way through the natural gas-processing industry, but the outlook doesn't appear good. Gas liquids must also compete with crude oil on another level. As charge stocks for olefin plants, ethane, propane and some butanes (Fig. 4) must compete with paraffinic streams, naphthas, and gas oils from refineries. Over 90% of the ethane from gas processing has been going to ethylene plants and accounts for more than 50% of the ethylene produced in the U.S.

Feedstock competition for ethane has not been a factor in recent years even though a spate of heavy oil crackers was built in the 1970s. Most of these subsequently had to add ethane and propane cracking capability as these lighter liquids became attractive feeds with the soaring price of oil in the late 1970s. Cracking of LPgas also avoids production of copious amounts of by-product olefins, such as propylene and butadiene or aromatics, which may be undesirable.

For this reason, ethane and propane to a degree should remain major olefins plant feedstocks but will be in a battle with the refinery distillates and could lose market share. Producing or not producing ethane is an option gas processors have. Ethane can be left or reinjected in the natural gas and sold as fuel. The problems for the transporters, however, mount as propane and heavier components are left in the natural gas. Therefore, many gas-processing plants will have to be operated for technical reasons even if the economics don't justify that.

The increase of one plant in the U.S. and stable capacity reported this year hides the fact that gas-processing plants are being added and shutdown. For example 23 were shutdown in Texas during 1985. The majority of them had capacities of less than 5 MMcfd and produced only debutanized gasoline or raw NGL mix. Of these, nine were small "white oil" plants in the Texas Panhandle that were shutdown in 1985 as a result of a Texas Railroad Commission order.

This controversial processing which produced natural gas liquids by refrigeration or high pressure was initiated because oil and gas rights are held separately in some Texas fields. Certain oil producers were claiming that

Table 4

## World gas-production trends (billion cu ft)

| | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | % Change 1985 vs. 1983 |
|---|---|---|---|---|---|---|---|---|---|
| United States | 19,922.4 | 19,999.4 | 20,267.0 | 19,596.0 | 18,731.0 | 16,581.0 | 18,068.0 | 17,304.0 | −4.2 |
| Western Europe | 4,793.7 | 6,866.6 | 6,668.7 | 6,906.6 | 6,142.1 | 6,383.5 | 6,795.4 | 6,647.2 | −2.2 |
| Canada | 3,133.1 | 3,646.5 | 2,668.3 | 2,623.0 | 2,546.1 | 2,414.1 | 2,651.8 | 3,350.6 | +2.6 |
| Latin America | 2,533.5 | 2,610.0 | 3,297.5 | 3,227.0 | 3,071.5 | 3,340.5 | 3,451.8 | 3,443.2 | −0.2 |
| Middle East | 2,604.4 | 1,624.7 | 1,221.3 | 1,542.0 | 1,799.7 | 1,633.0 | 1,533.5 | 1,723.7 | +12.4 |
| Asia-Pacific | 1,640.1 | 1,827.9 | 1,558.4 | 2,765.0 | 2,176.6 | 2,187.7 | 2,530.7 | 3,030.8 | +19.8 |
| Africa | 1,558.1 | 1,027.9 | 884.7 | 1,947.0 | 1,168.9 | 1,143.8 | 1,629.1 | 1,764.0 | +8.3 |
| Communist bloc and China | 17,683.3 | 19,591.4 | 21,069.9 | 19,210.0 | 20,258.0 | 21,383.0 | 23,272.2 | 25,457.9 | +9.4 |
| **World total** | **53,868.6** | **57,194.4** | **57,635.8** | **57,816.6** | **55,893.9** | **55,066.5** | **59,932.3** | **62,721.4** | **+4.6** |

Source: International Petroleum Encyclopedia, 1986, PennWell Publishing Co.

Table 5

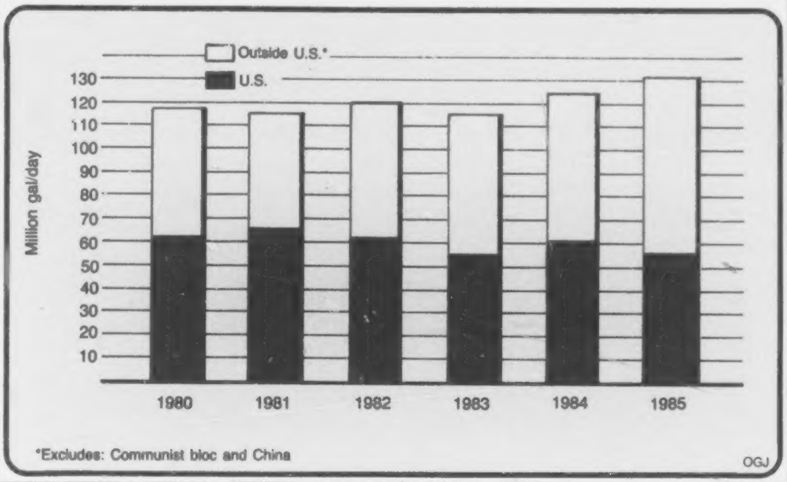
## World's 20 top gas-producing countries in 1985

| Country | Production, $10^9$ cu ft | Share, % |
|---|---|---|
| U.S.S.R. | 22,697.9 | 36.2 |
| United States | 17,304.0 | 27.6 |
| Canada | 3,350.6 | 5.3 |
| Netherlands | 2,858.8 | 4.5 |
| United Kingdom | 1,497.1 | 2.4 |
| Algeria | 1,320.0 | 2.1 |
| Mexico | 1,312.2 | 2.1 |
| Romania | 1,200.0 | 1.9 |
| Indonesia | 1,056.0 | 1.7 |
| Norway | 902.2 | 1.4 |
| Argentina | 667.3 | |
| West Germany | 608.1 | |
| Italy | 448.9 | |
| Venezuela | 609.6 | |
| Australia | 473.7 | |
| China | 600.0 | 7.5 |
| Iran | 480.0 | |
| Pakistan | 355.3 | |
| Brunei | 300.0 | |
| France | 190.7 | |
| Top 20 | 58,232.4 | 92.8 |
| Others | 4,489.0 | 7.3 |
| **Total** | **62,721.4** | **100.0** |

Source: International Petroleum Encyclopedia, 1986, PennWell Publishing Co.

Fig. 2

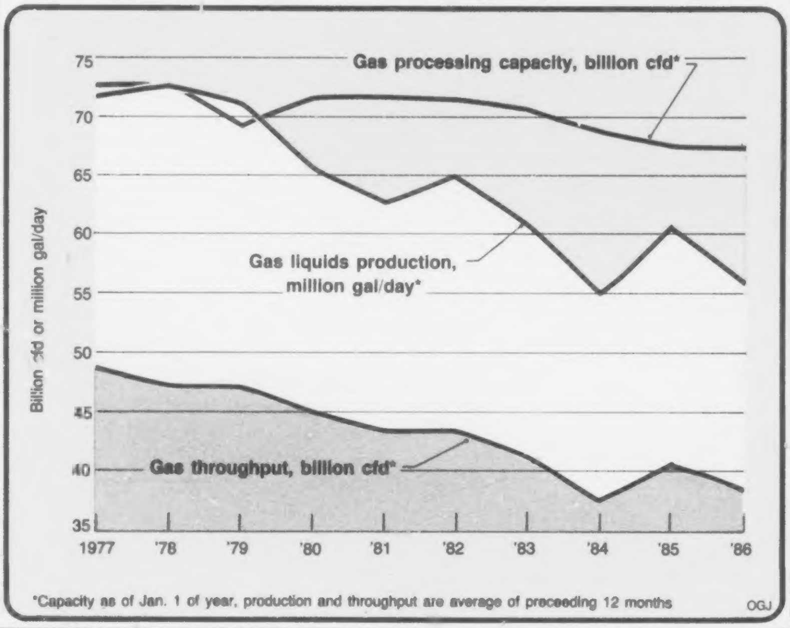
## U.S. losing dominance in gas liquids output



*Excludes: Communist bloc and China

Fig. 3

## Trend lines are down in U.S. gas processing



*Capacity as of Jan. 1 of year, production and throughput are average of preceeding 12 months

this NGL was oil coming from " oil wells" which enjoyed some additional benefits from not being regulated.

**States.** Texas and Louisiana far outstrip any other states in the U.S. with gas-processing capacity and throughput. However, both logged decreases in throughput and capacity during 1985 with Texas regaining the lead over Louisiana.

Texas, however, dominates in the production of NGL, producing more than twice as much as Louisiana.

Michigan in the past several years has come out of no where to become a growing factor in the gas-processing industry. The number of plants, capacity, and throughput have all leaped this year. This is a case of improved oil-finding technology leading to more gas-processing plants. There have been some phenomenal successes on Michigan's Niagaran reef trend that sweeps northeastward from Lake Michigan to Presque Isle County on Lake Huron. Oil and gas completions have given the state's reserves big boosts and they are now being exploited. Alaska should surge into the top ten in the next couple of years with the completion of a major plant at Prudhoe Bay. Table 2 also shows the top ten states account for 93.5% of the gas throughput and 93.2% of total NGL production.

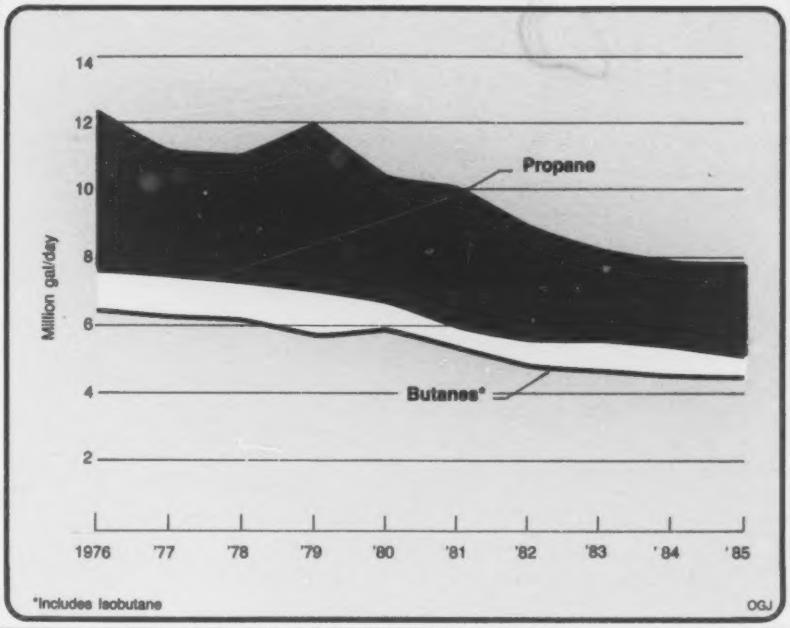
**Outside U.S.** Canada chalked up some solid gains in several important categories with increases in throughput and liquids production (Table 1 and Fig. 5). Canada with the province of Alberta leading the way has been adding plants and capacity at a rapid clip since 1984. Fifty-seven plants have been added bringing in with them 3,300 MMcfd of capacity.

The rest of the world outside the Communist bloc also revealed some good gains, growing 3.7% in gas throughput, and 5% in gas liquids production. Latin America led the way with a major gain in Venezula. Corpoven added two plants, each of 800 MMcfd capacity, in Anzoategui. Corpoven has extensive ethane recovery capabilities.

**Gas-plant construction.** Table 3 reveals the downward trend in gas-processing plant construction. But there are still some major projects under way. One of the biggest is ARCO's 3,000 MMcfd plant for Prudhoe Bay.

Fig. 4

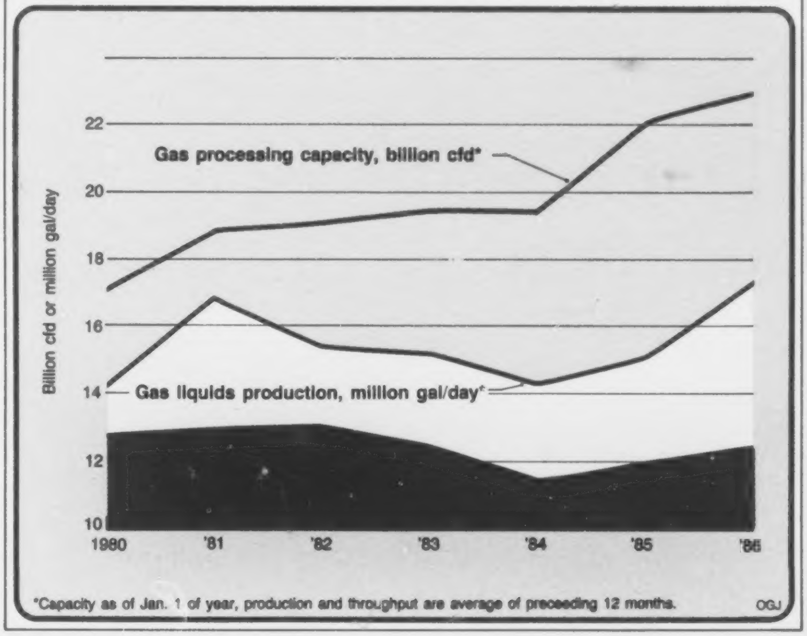
Production of key products in U.S.



*Includes isobutane

Fig. 5

Canadian gas processing moving up again



*Capacity as of Jan. 1 of year, production and throughput are average of preceeding 12 months.

That is due for completion in mid-1987. Conoco and Tenneco are also heading for completion of a 500 MMcfd plant at Farmington, N.M. The U.S. construction scene is also sprinkled with carbon dioxide recovery plants for enhanced oil recovery operations. Six of the plants are in Texas; one, being built by Shell Western E&P, is in Mississippi.

Overseas, Venezuela will get another hefty addition of capacity when Meneven completes its 800 MMscd San Joaquin plant. That was scheduled for completion last month.

There are projects in the 500 MMcfd range by Cogasco in Argentina, Pemex in Mexico, Amoco in Sharjah, and Shell U.K. in Scotland. The U.S.S.R. is to complete a 630 MMcfd plant in Astrakhan this year.

Table 6

## World's major gas reserves (as of Jan. 1, 1986)

| | Estimated proved reserves $10^{12}$ cu ft | Share,% |
|---|---|---|
| U.S.S.R. | 1,500.0 | 43.1 |
| Iran | 470.0 | 13.5 |
| United States | 197.0 | 5.6 |
| Qatar | 148.0 | 4.2 |
| Saudi Arabia | 121.0 | 3.5 |
| Algeria | 107.0 | 3.1 |
| Norway | 104.0 | 3.0 |
| Canada | 99.7 | 2.9 |
| Mexico | 77.0 | 2.2 |
| Netherlands | 67.1 | 1.9 |
| Venezuela | 59.1 | 12.5 |
| Malaysia | 52.7 | |
| Nigeria | 47.0 | |
| Indonesia | 36.6 | |
| United Kingdom | 33.0 | |
| Kuwait | 32.5 | |
| China | 30.0 | |
| Iraq | 29.0 | |
| Argentina | 23.6 | |
| Libya | 21.4 | |
| Abu Dhabi | 20.5 | |
| Australia | 18.2 | |
| India | 16.9 | |
| Pakistan | 15.4 | |
| **Subtotal** | **3,326.7** | **95.5** |
| **Others** | **157.4** | **4.5** |
| **Total** | **3,484.1** | **100.0** |

Source: OGJ, Dec. 30, '85, pp. 66-67

**Sulfur construction.** Sulfur recovery plant construction is moving forward on a truly international scale. Western Europe and Canada are deeply concerned about acid rain and there is great stress on cleaning up effluents containing sulfur and nitrogen compounds. However, many major projects are going up outside these industrialized areas (OGJ, Apr. 28, pp. 85-86). Kuwait National Petroleum has major sulfur recovery projects slated for completion this year and next at Ahmadi and Mina Abdulla, Kuwait. Capacity will be for some 800 ton/day in three plants. There will also be associated tail-gas-treating units.

Saudi Arabia plans 300 ton/day sulfur recovery units at Al Quasim and Ras Tanura. The biggest project is in the Soviet Union in Astrakhan where it is reported that four sulfur recovery lines will be completed this year with a total capacity of 8,000 ton/day. A 1,580 ton/day plant is due to startup at Tenguiz in 1988.

**World gas.** In spite of dips in production in a couple of regions, the worldwide production of natural gas continues on an upward trend (Tables 4 and 5). At the right price, natural gas is a premium fuel. As long as it will be possible to get a higher price for gas components that have been extracted, then gas processing will continue as one of the world's major energy operations. ▪

Vickers
SELF SERV
REG.
PER GALLON
.99⁹
PEPSI

**Vickers self-serve station** in Denver is one of about 450 retail outlets that Total Petroleum Inc. owns and operates to sell premium unleaded and other grades as competition among marketers intensifies.

# Hot premium unleaded gasoline demand fires marketing blitz by U.S. refiners

**Michael Obel,** Staff Writer
**Bob Williams,** Senior Staff Writer

Strong margins and growing demand for premium unleaded gasoline are heating competition among U.S. refiners and marketers.

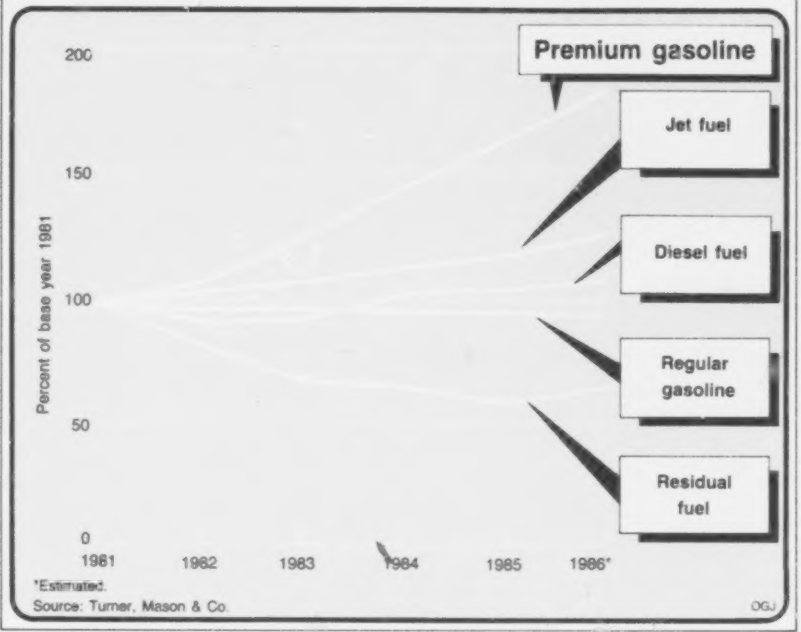
The demand increase reflects two trends. One is new vehicles' needs for higher octanes and more additives that prevent multiport fuel injector fouling. The other is gasoline prices so low that drivers this summer can buy premium unleaded for less than what they spent on lower quality grades last summer.

In a battle for premium unleaded market share, major oil company marketers are spending heavily on advertising stressing gasoline quality. Blenders, marketers, and independent refiners have been quick to engage in oneupmanship.

The renewed emphasis on product quality has spurred gasoline detergent sales. Ethanol interests, too, are adding detergents as they bid for a slice of the growing premium unleaded market.

A major challenge for refiner/marketers is to anticipate consumer octane demand in the wake of the Environmental Protection Agency's lead phasedown program. By Jan. 1, 1988, EPA may effectively eliminate the use of lead in motor gasolines. The limit was reduced to 0.10 g/gal last Jan. 1, but refiners are using more to the extent

## How U.S. products demand is changing



*Estimated.
Source: Turner, Mason & Co.

that they have access to lead banking rights. One likely option is an 89 octane (R + M/2) grade, which some majors are testing in selected markets. More tests are likely before such a midgrade is established as a regional or national option, along with regular and premium unleaded grades.

The recent emphasis on marketing reflects a widely held industry view that for the next 3-5 years U.S. downstream operations will be more profitable than exploration/production.

**Demand growing.** Trends underlying premium unleaded's demand growth show changes in consumer buying habits.

Now that prices have dropped, some drivers are willing to pay more for a product they believe will reduce engine knock and otherwise improve performance, says Robert E. Cunningham of Turner, Mason & Co., Dallas consultants.

"Even though there is apparently limited short term elasticity in total gasoline demand, there seems to be an internal elasticity that has created fuel switching to premium unleaded," he says.

"It appears that the absolute top price for some customers outweighs the relative price, encouraging them to substitute a higher quality with less total gasoline expense than they had last year."

The growth in premium unleaded sales has been evident for several years (see chart).

"Although no current statistics are available, premium unleaded demand is approaching 20% of the pool this year," says Cunningham. The increase in the share of premium grades would be steeper still if not for the decline in demand for premium leaded.

Premium unleaded had 15% of the total pool in 1984.

The fact that premium unleaded offers refiners and marketers their best margins of any gasoline grades explains the current advertising blitz. It's likely to continue for several more years.

"By 1990, we expect continued growth to push the demand for premium unleaded to 30% of the gasoline pool," says Cunningham.

Turner, Mason's figures are confirmed by marketers.

Shell Oil Co. reports that from the introduction of its SU2000 premium unleaded grade in the spring of 1984 through June 1986, the premium unleaded share of Shell's total gasoline sales increased by 8 percentage points.

Mobil Oil Corp. says sales of its Super Unleaded Plus, introduced in September 1985 as its new premium unleaded grade, are steady at levels about 35% greater than they were on average in 1985.

And Amoco Oil Co., which with premium unleaded sales of more than 2 billion gal/year is the largest U.S. marketer of that grade, expects its 1986 premium unleaded sales to increase 3-5% from a year ago, says Bob Gamrath, business manager for light oils marketing.

**Unocal's experience.** Unocal Corp.'s experience in switching from premium leaded to premium unleaded demonstrates how strongly demand for premium unleaded demand is growing.

Recently, Unocal was the only major company on the West Coast offering premium leaded gasoline. It never sold a premium unleaded grade.

This spring the company began to phase out premium leaded and offered premium unleaded.

"Our sales of premium leaded had declined during the 1970s, and we were expected to be out of the market for it before now," says Dennis Lamb, Unocal general manager for western marketing and administration. "But premium leaded sales held up remarkably well, perhaps with all the attention and publicity from lead phasedown, so we kept the lion's share of a small market."

But lead phasedown and higher octane needs from modernization of the auto fleet caught up with Unocal, which wants to remain a two product marketer.

The company also sells a midgrade (89) unleaded.

In April Unocal dropped leaded premium and introduced unleaded premium in Washington and Oregon. Premium leaded's percentage share of Unocal's Pacific Northwest gasoline pool had been 20-22%. Premium unleaded now accounts for 28% of that market.

Unocal is switching to unleaded from leaded in Nevada and will make the same conversion in California later this month.

It will make the conversion official Aug. 1 with point-of-sale and television advertising.

For former premium leaded buyers concerned that unleaded gasoline might damage older engines, Unocal also is introducing a new product, Valve-saver, which it says will eliminate valve recession in older cars without boosting octane or leaving valve combustion products.

**Majors push quality.** The accent on quality is the majors' weapon of choice in the battle over premium unleaded market share.

The decision by Amoco to introduce its premium unleaded Ultimate grade last month was a move to protect its leading position in the premium unleaded market.

"The demand (for premium unleaded) is up, and, obviously, we want to get a piece of that demand increase," says Gamrath.

Amoco's advertising for Ultimate stresses a special additive that contains an antioxidant, a detergent, and a corrosion inhibitor, as well as the

FULL SERVE
FULL SERVICE

**Full service station** is one of the options Phillips 66 Co. is pursuing to boost brand loyalty among customers, who have become more willing to pay extra for higher quality gasoline.

fact that it has more than 25 specifications.

In the eastern U.S., Ultimate will post a 93 octane rating, in the Midwest a 92 rating.

One indirect way companies are stressing quality is improving and standardizing the appearances of service stations.

Charlie Bowerman, Phillips 66 Co.'s marketing vice-president, credits 3 years of investments in 24 cities where it is building its "Pacesetter Stores" with Phillips' 30% increase in motor fuels sales.

To encourage upgrade of retail outlets, Phillips offers its 1,700 independent marketers incentives to build new outlets or rebuild or remodel existing outlets to Phillips' specifications.

Phillips pays part of the cost of the building materials, landscaping, advertising, and other image-related expenses.

Phillips marketer Steve Cady of Peoria, Ill., says, "If you don't have the image, you probably don't have the business."

**Other marketing attitudes.** Not all major U.S. companies are ready to jump on the premium unleaded bandwagon.

Major refiner/marketers on the West Coast, such as Atlantic Richfield Co. and Chevron Corp., aren't trying and don't envision special promotional efforts to boost sales of premium unleaded vs. other grades of gasoline.

But both hew carefully to industry's emphasis on quality.

Chevron, for example, isn't interested in introducing a product or launching a separate promotional campaign to capitalize on the premium unleaded demand boom.

Its last new product entry was an ill-fated "super" gasoline introduced briefly in 1959.

But in the last 2-3 months the gasoline marketing emphasis of Chevron has stressed its Techroline additive. The compound is injected into all unleaded grades.

At the same time, it won't ignore the new opportunity for premium unleaded.

"We're trying to make retailers aware of the potential for the premium product," says Chevron marketing executive Jack Maguire.

"Refiners are just trying to suggest that there are three grades in a retail package and telling retailers to focus on that mix."

ARCO is more succinct.

"We have no plans to develop new products in response to fuel injection problems and no plans to promote premium unleaded," an executive says.

**How independents keep up.** The premium unleaded media blitz by majors is pulling smaller integrated oil companies along in its wake.

An increasing number of marketers with refining capacity are finding ways of pushing quality, too.

Many small integrated companies are blending off-the-shelf detergents into their premium unleaded grades and renaming them or advertising the fact that they contain detergents.

At least two independent Texas refiners are planning to add detergents to their premium unleaded grades, and at least one plans to rename its top grade as part of an advertising campaign.

The biggest cost, and the greatest amount of time required, in adding detergents to premium unleaded comes with installing the injection systems at terminals. Cost of installing a grassroots system is $20,000-40,000.

Like the majors, small integrated companies are redoing their retail outlets.

Diamond Shamrock Refining & Marketing Co. this year launched a $150 million program to double its retail gasoline sales by 1991. Special efforts will be made in Dallas, Fort Worth, San Antonio, Austin, Corpus

Christi, Denver, and southern Louisiana.

At the center of the campaign is improving the appearance of outlets.

The company is considering remodeling 35-40 units/year for 5 years, "plus some possible acquisitions in these main areas," a Diamond Shamrock official says.

The new units will be convenience stores covering 1,200-1,600 sq ft with 12-16 pumps. All the new units will be owned and operated by Diamond Shamrock.

This year the company plans to build 35 new high-volume outlets with convenience stores, rebuild an additional 20 units, and remodel another 20.

**An example.** One small, independent refiner/marketer is carefully targeting its customers.

"Our customers are in the 18-45 year range," a manager of the company says.

"We're starting a limited advertising campaign on radio, billboards, and on buses. We're not using TV because our customers listen to more radio than they do TV."

To counter one major's recent introduction of a premium unleaded grade with a detergent additive in a large city, the independent announced it already was using a detergent. Furthermore it already was using that detergent in both its unleaded grades, not just premium unleaded.

The rewards of such precise strategy and marketing oneupmanship, however, are modest for independents that want to slug it out with majors in metropolitan markets.

"We'd like to at least maintain our market share, and if we do that we have gained because the majors are nipping away at us," the manager says.

"It used to be, 5-10 years ago, they'd let us have a penny or a penny and a half on the street. Now they are fighting on the street with cash only discounts for leaded regular.

"You go after them with what you do better than they do. We can act quicker. We can make decisions faster."

**Chain marketers.** The view that independents must capitalize on their responsiveness if they are to succeed is echoed by Ken Doyle, executive director of the Society of Independent Gasoline Marketers of America (Sigma).

"Retail gasoline marketing runs on paper-thin margins," Doyle says. "A quarter of a cent price change will dictate a total change in where you purchase your product."

Independent marketers and jobbers continue to be squeezed hardest in metropolitan markets.

As a result, they look at rural and small communities for growth. But those arenas are often picked over.

More than 12 months ago one marketer with 14 convenience stores offered $2,500 to any employee who spots a location on which he could build and profitably operate a new convenience store.

He has yet to receive his first suggestion.

Marketers that can't afford to expand as rapidly as major companies tend to place more emphasis on margins than on the amount of gasoline sold.

"Gallons don't mean anything if there are no profits," says Jack Griffith, president of Griffith Petroleum, Stillwater, Okla. "I don't have a single banker that buys gallons. They want profit."

**Detergent makers.** Manufacturers of gasoline detergents and additives report dramatic boosts in sales of their products to gasoline blenders and producers.

Vince Hanlon, senior product manager in Ethyl Corp.'s petroleum additives division, says that 3-5 years ago gasoline detergents were a 6-8 million lb/year business.

"In the short term it is moving rapidly to a 20-30 million lb/year level. In a year or two it should settle back some to a 14-18 million lb/year business."

The dosage of detergents varies greatly, from as low as 10 lb/1,000 bbl of gasoline to more than 50 lb/1,000 bbl.

While some detergents are added at the refinery, most marketers inject them at terminals.

Gasoline detergent sales are likely to keep growing since the Renewable Fuels Association (RFA) secured commitments from U.S. fuel ethanol producers and distributors to begin using their ethanol as a carrier for a detergent.

The commitments come from companies that account for about 92% of the fuel ethanol sold in the U.S., or more than 7% of the nation's fuel supply. The RFA move represents the largest program to date to provide detergents in gasoline.

"We are responding to a request from General Motors and other auto manufacturers to clean up the nation's gasoline," says Art Stuenkel, RFA chairman.

"General Motors contacted the RFA in May and asked that the ethanol industry consider adding detergent to ethanol as a means of providing port fuel injection deposit prevention in many of the independent brands of gasoline."

Following a series of meetings last month, the RFA voted to use ethanol as a carrier of detergents at 10 times the normal concentration," he says.

Domestic ethanol producers worked with a division of DuPont Chemical to develop the package.

"When the ethanol is blended with gasoline in the normal 10% ethanol to 90% gasoline ratio, the finished blend will contain an adequate level of detergent to keep fuel injectors and carburetors clean," says DuPont's Dr. Perry Polss, senior supervisor in the petroleum additive division.

**How prices changed.** The usually stable price differential between premium unleaded and regular grades widened this year.

The big fall in crude oil prices cut incremental gasoline octane costs via catalytic reforming by 50% to less than 0.5¢/gal/octane.

However, gasoline demand and increased clear pool octane requirements have offset this reduction entirely, says Turner, Mason's Cunningham.

With the greater than expected increase in overall gasoline demand in 1986, coupled with the EPA's lead use restrictions, refiners have had to push their octane production capacities to the limit. In many cases, octane costs rose steeply.

"Early in the second quarter many refiners decided that the wholesale price increases they were going to have to institute to cover their sharply increased octane costs, due to both increased demand and increased pool octane, would be disproportionately attached to premium unleaded," says Cunningham.

"The upshot was a price spread increase from 4¢/gal to as much as 7¢/gal between premium and regular grades—exactly the opposite of what one would expect from the unprecedented crude oil price collapse."

Turner, Mason expects the premium-regular price differential to be about 4-6¢/gal in 1986-87, even with crude oil selling for $15/bbl.

**Outlook.** Demand for premium unleaded could fluctuate in the years ahead, depending on further EPA rule changes on lead phasedown as well as gasoline volatility, says Lew Gibbs, Chevron Research Co. senior engineering associate.

How the EPA rules shake out will influence the mix of gasoline grades and octanes and prospects for gasoline additives, detergents, and alcohol fuels.

Gibbs sees two possibilities, based on projected octane requirements, for an all-unleaded gasoline market in 1988 vs. 1980-86. In one, regular leaded is replaced by a middle octane

## ARCO departs from tradition to accent fast food profits

Prospects for increased profits in retail marketing have persuaded Atlantic Richfield Co. to go beyond major companies' usual emphasis on conventional downstream operations.

ARCO's added step in downstream diversification is apparent in advertising in trade and business publications by the U.S. West Coast's biggest gasoline retailer.

A recent ad featured a photograph of a two for 99¢ hamburger with the caption, "The New ARCO." It referred to ARCO's recent expansion of fast food services at its am/pm minimart convenience store/service station chain.

That ad and other aspects of ARCO's am/pm marketing push are clear signals to competitors and the investment and lending communities that the company is in the fast food business to stay.

The goal, in a parting with tradition, is to make a profit on fast food sales rather than use fast food as an attraction to sell gasoline.

It's always been a given that a service station's gasoline sales determine its profits. And regardless of the marketing approach, most gasoline marketers with convenience store sales still emphasize gallonage as the key to profits.

But that is changing among major and independent gasoline retailers.

**ARCO's rationale.** ARCO's move into convenience store and fast food sales is an effort "to go in a completely new direction, to build an operation beyond the gimmicky kind of marketing we've seen downstream in the past," said Al Greenstein, ARCO western region media relations manager.

ARCO began devising an approach for entry into the fast food business even before its trend-setting 1985 restructuring and the 1986 plunge in oil prices.

"Even though we had two back to back 1 billion gal sales months, we saw gasoline demand ultimately flattening out," Greenstein told Oil & Gas Journal.

"At the same time, we realized that the convenience store was another profit center, as significant as the service station itself. Although gasoline revenues were higher, we learned that more than half of the dealer's gross profits came from am/pm store sales."

That realization prompted ARCO to shift its view of an am/pm store from that of an outlet to sell gasoline to that of a property investment. Hamburgers, hot dogs, and ice cream are just other efforts to maximize that investment.

**Independents agree.** Independent marketers increasingly have been venturing into convenience store operations. Their aim is not only to boost gasoline sales but to enhance return on a real estate investment of $300,000-500,000/store, said Ken Doyle, executive director of the Society of Independent Gasoline Marketers of America.

"You have to do a very good volume of gasoline sales to make that investment cost-effective," Doyle said.

"There are those who are doing it for gallonage and those for diversification. When my members look at a site they evaluate its income potential from all sources. The cash flow is a function of all products available."

**Hamburger wars?** So some independent gasoline marketers soon may be competing with ARCO in fast food sales. And the gasoline price wars among gasoline retailers of recent years may give way to hamburger price wars.

ARCO is selling more than 500 hamburgers/day at each of its am/pm stores, thanks to the two for 99¢ promotion.

That kind of success has prompted Wendy's, a national restaurant chain, to offer its own hamburger deal in Los Angeles—three for 99¢. And McDonald's, a fierce competitor for America's fast food dollars, is opening a big new restaurant next door to ARCO's highly successful am/pm at Los Angeles International Airport.

"We're taking on McDonald's and Wendy's, people whose business is food sales," Greenstein said.

There is bound to be more diversification downstream, just as the petroleum industry diversified into other upstream resources when energy prices, mainly for crude oil, were expected to continue soaring, Greenstein figures.

"More and more oil companies are looking for profits downstream, looking at refining and marketing for profitability," Greenstein said.

"When you're already in retail gasoline sales, selling hamburgers and whatever else isn't such a big leap."

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(89) unleaded grade. In the other, regular leaded would be replaced by a suboctane (85) unleaded.

Regular unleaded will become marketers' fighting grade, or loss leader, with the best margins on premium unleaded and perhaps later on midgrade unleaded.

Amoco's Gamrath says his midgrade tests in Florida "are going very well." Other tests may begin this fall in the Midwest and in the Northeast, he says.

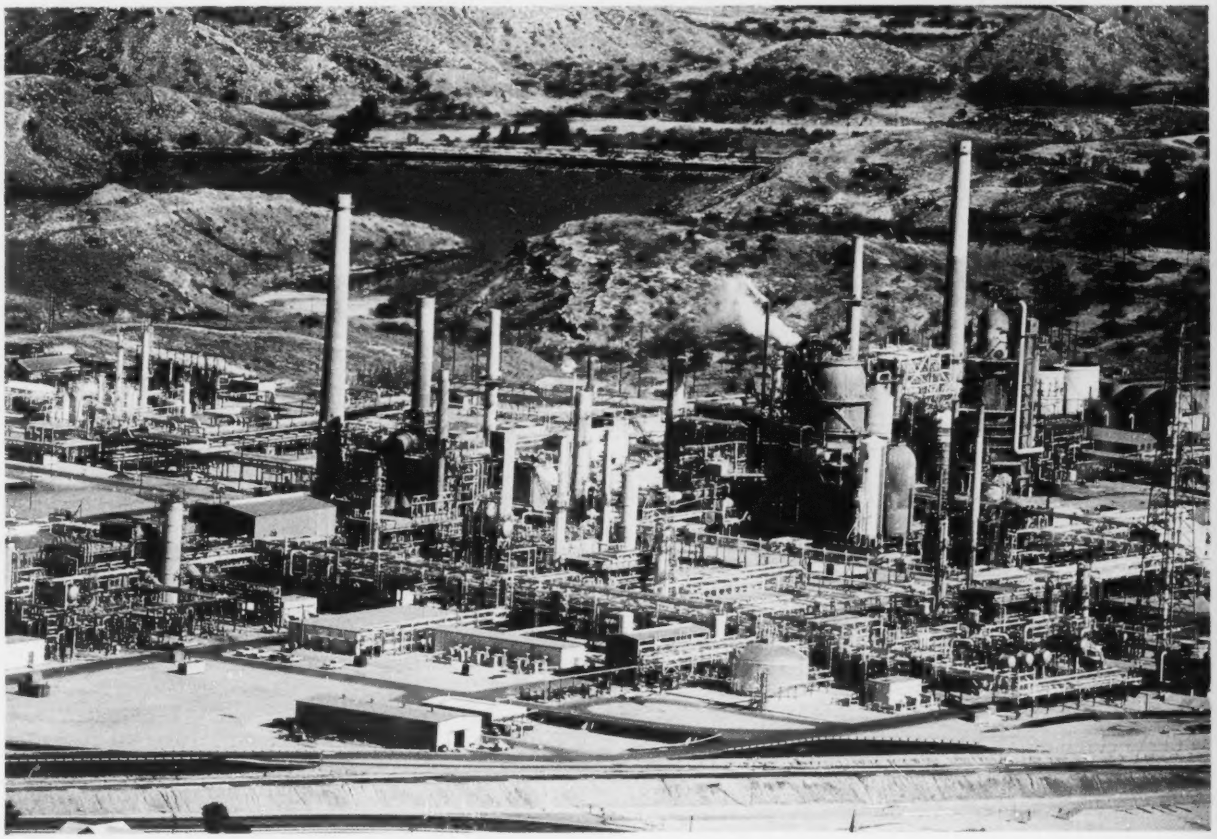
Jobbers and chain marketers are not expected to have any problems offering their customers a midgrade.

"It will come down to buying an 87 octane product and a 90 octane product and blending them for a midgrade," says Sigma's Doyle.

"If you're in a state that offers sufficient tax exemptions for ethanol you're going to buy an 84 octane product and add ethanol to get an 87 octane product. That will be your low grade. Then you're going to take an 89 octane product and add ethanol for a 91 or a 92 octane product. So you will have all three grades, the 87, the 89, and the 92."

Finally, the success of the latest efforts by majors to create brand loyalty has yet to be determined fully. The current campaigns differ from similar efforts in the 1960s, when the same companies sought to generate brand loyalty but did so by offering full service.

"Whether brand loyalty can be established now only by advertising a better gasoline in a self-service pump remains to be seen," says Doyle. •



**Refinery** in Borger, Tex., owned and operated by Phillips 66 Co., enjoys strong margins because of healthy demand for its slate of light, highly valuable products.

# Mix of reasons underpins rise in downstream U.S. earnings

**Michael Obel,** Staff Writer

A wide range of causes underpin the strong earnings performance among U.S. refiner/marketers during first half 1986.

For most refiners the crude oil price collapse was a curse in the first quarter and a blessing in the second quarter.

What effect it has on the calendar year remains to be seen, but few U.S. refiners say that the crude oil price collapse is the fundamental cause of their recent surge in profitability.

"My guess is that, if you take out all the last in, first out accounting, refiners will actually have a less profitable year in 1986 than they had in 1985, when you consider inventory writedowns," says Roger R. Hemminghaus, president of Diamond Shamrock Refining & Marketing Co., San Antonio.

Still, the first half earnings reports of U.S. petroleum companies showed a big surge in refining/marketing margins vs. an upstream collapse.

For example, Mobil Corp. reported a 69% drop in U.S. exploration/production earnings for first half 1986 compared with a 426% rise in U,S. refining/marketing earnings for the same period.

## Conoco's Ponca City refinery program revives margins

Recent changes at Conoco Inc.'s Ponca City, Okla., refinery typify how many U.S. refineries have gone from weak links in oil company operations to strong performers.

More than a year ago, the company decided that the refinery and its related businesses had to achieve $24 million in after tax operating income, a 15% return on liquidation value.

One route to that goal entailed cutting the refinery's operating costs by $10 million/year (OGJ, July 29, 1985, p. 64).

Failure could have meant closing the plant.

This summer, however, the threat of closure was lifted as the refinery and its businesses met all goals.

**Key strategies.** Gary Edwards, Conoco vice-president for refining, marketing, and transportation, outlined some of management's key strategies.

"One was to change the way crude oil was purchased, from a major posting basis to a program that was more responsive to the spot market. Also, we decided to reduce working capital charges by reducing the level of inventories of crude oil and product at the refiner and throughout the distribution system."

Increases in after tax operating income and how they were achieved break out as: $21 million, purchasing crude on a more market responsive basis; $11 million, increasing margins between crude prices and product prices; $5 million, running cheaper, poorer quality crudes with better margins; $4 million, operating with lower crude inventories to give crude traders more buying flexibility; $4 million, increasing crude runs to improve productivity; $3 million, reducing operating costs by about 10% from 1984 levels, mostly achieved by a 14% cut in personnel; and $2 million, blending gasoline with lead and manganese additives more efficiently, plus buying cheaper coker feedstocks.

In addition, efforts to reduce working capital charges resulted from a reduction of refinery crude oil inventory to just a 1 day supply.

Although the inventory reduction did not directly help earnings, it did improve the return on liquidation value by reducing the refinery's asset base.

As such, it had the equivalent effect of an additional $5 million in earnings.

"As can be seen, 80% of the improvement came from the efforts of Conocoans as opposed to a fortuitous market change," Edwards says.

Exxon Corp. reported U.S. exploration/production earnings for first half 1986 of $429 million, down $721 million from the same 1985 period, and the company's U.S. refining/marketing earnings increased $277 million to $357 million.

Even when refining earnings suffered in the first quarter, owing to softer wholesale product demand in hopes of still lower prices, retail marketing divisions buoyed overall earnings with strong margins. The reverse was true the following quarter.

The reason is market volatility. In a declining market, the product price, whether retail or wholesale, that falls most quickly causes the most damage to earnings. When product prices rebound, the situation is reversed.

So it behooves companies to seek a balance between their refining output and retail product sales.

Volatility in crude oil markets makes it especially important when a refinery's crude supply is priced. Netback schemes guarantee a margin by allowing the buyer to set the price after product sales.

U.S. company executives are reluctant to speculate on the ultimate downstream impact of netback crude pricing. But netback deals in Europe have encouraged crude runs that can't be justified by the current products market there. With product stocks burgeoning there as a result, there are signs that intensified retail price cutting might again be in the offing (OGJ, Aug. 18, p. 26).

Whether that happens in the U.S. remains to be seen.

Nevertheless, the oil price rollercoaster mandates an eye to timing of crude pricing. So U.S. refiners that don't have netback crude deals are taking other steps that offer similar advantages or give them influence over when the crude price is set.

Such measures are paramount because they help protect refiner/marketers from what is currently their worst enemy: crude and product price volatility.

**First quarter crunch.** Exploration and production divisions were not the only operations hurt by the crude oil price collapse.

"When prices began to collapse in the first quarter, most refiners saw a squeezing of their margins," says Hemminghaus.

That's because the anticipation of prices falling even further caused jobbers to hold back from purchasing products. That in turn made product prices fall, in some cases more rapidly than crude prices, he says. And when the crude price stabilized in the second quarter, wholesale prices firmed, reviving refining margins.

Many refiners who didn't have the cushion of guaranteed margins from netback crude deals now regret not taking full advantage of the futures market to protect themselves from further slides in crude prices.

"Most of us were running along in a dream world thinking, 'There is no way it's going to collapse to any $15/bbl'." one refiner recalls.

"We as a company did some hedging in the New York Mercantile Exchange, but not as much as I would do today if I were in similar circumstances."

In addition, refiners who obtained their crude on the spot market were hurt more by the crude price collapse than refiners who obtained their supply on a posted price basis.

That's because the price of spot crude is set before the price of posted crude, the value of which is determined at the time of lifting—not at the time the contract is signed.

Mapco Petroleum Inc.'s Gaylon H. Simmons, vice-president of crude and products supply, says that in a falling market a crude acquisition policy based on posted prices will be less costly than one tied to spot market values set in advance of the processing month.

"In the spot market approach, the price of the crude oil you buy for a given month is set in the preceding month," he says. "In a falling market, that's bad news.

"But in a posted market approach, the price of the crude oil is set at the time of lifting which will be several days or weeks later than the preceding month."

In a rising crude market, the opposite would be true: the least costly position is the one that calls for the price to be set as early as possible.

The crude price collapse also drove refiners to make a number of changes in the way they operated their plants.

Mapco had scheduled a plant wide turnaround at its 60,000 b/d Memphis refinery for last March. However, it moved the project up to mid-February to help minimize inventory losses from the crude price collapse.

**Second quarter rebound.** In the second quarter refining margins rebounded because crude costs stopped falling and gasoline prices firmed owing to stronger demand.

Some refiners set record gasoline margins during the second quarter. For example, in May one large integrated U.S. oil company reported a record net wholesale gasoline margin of $8.40/bbl.

Another of the company's plants posted a $7.56/bbl margin in the same month. That margin was trimmed to $3.78/bbl in July because of product price weakening that began in June.

Strong gasoline demand has continued through the third quarter.

Weekly Oil & Gas Journal estimates show total U.S. products demand for the year to Sept. 5 up 3.2% from a year earlier. Motor gasoline demand for the same period is up 2.7% from the previous year.

Retail divisions generally did better in the early part of the third quarter than refining divisions as wholesale prices fell faster than retail prices.

"Early in the third quarter sales were slow due to destocking by jobbers and dealers waiting to buy their supplies," says Diamond Shamrock's Bob Mehall, vice-president, crude oil. "By August sales were increasing and they are still strong."

Hemminghaus says that scheduled conversion unit turnarounds in September and October will reduce production, which is expected to buoy margins to a "reasonably strong" level.

Early next month Diamond will begin a 2 week turnaround of a cat cracker at its 85,000 b/d Sunray, Tex., refinery.

Rather than go to the spot market to obtain gasoline to make up for the product shortfall in its retail network, Diamond is producing heavily this month and plans to borrow product from its exchange partners.

That decision underscores the company's view that ample products will be available in the months ahead.

**The seesaw.** Refiners are becoming used to the way marketing profits occur out of phase with refining profits.

"This year has been a wildly swinging year," says a major oil company executive. "The margins are moving from refining to marketing and back very rapidly."

Diamond's Hemminghaus says, "In the first quarter retail profits were strong and refining profits were bad. That's because wholesale prices were dropping fast while the retail price on the street was holding up longer."

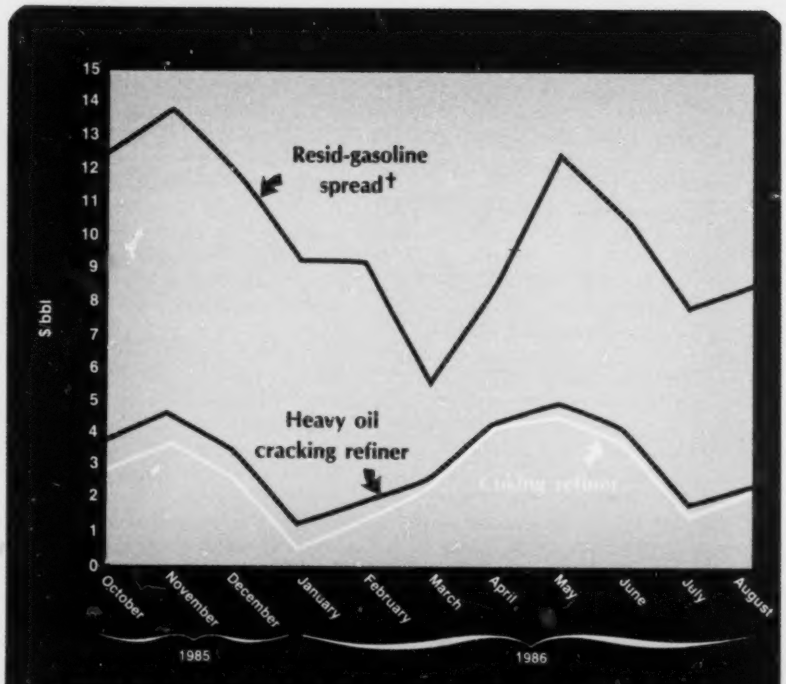
"When refining margins improved in the second quarter...retail prices were not improving fast enough and so retail saw a squeeze."

The volatility of prices and the way in which retail and wholesale profits move out of phase with one another have contributed to a renewed oil company interest in marketing.

A network of efficient, high volume retail outlets allows downstream managers to recoup refining losses that occur whenever wholesale prices weaken.

Mapco, for example, is seeking to balance the gasoline output of its Memphis refinery with its retail sales, primarily by building or buying high volume, convenience store outlets.

The company has increased to 80% the amount of gasoline produced at its Memphis refinery that it sells directly through retail outlets.



*Cash margins based on dealer tank wagon prices and an average 86% utilization rate for a 150,000 b/sd, high complexity U.S. Gulf Coast refinery. †Wholesale price differential between high sulfur resid and unleaded regular gasoline.
Source: Chem Systems Inc.

**Price relationships unchanged.** Refiners say that despite the crude oil price collapse, most product price differentials haven't changed significantly.

That's important because it allows refiners to continue pursuing the investment and operating plans based on those differentials that they devised before the collapse.

"As far as we're concerned, all the relationships have held," says Pete Dimond, manager of Conoco Inc.'s 134,000 b/d Ponca City, Okla., refinery.

That perception is supported by a Turner, Mason & Co. study that concludes that product price differences have remained as stable through the 1986 crude oil price collapse as they have for the last two decades.

The consultant says that product price differentials seem to vary with the price of No. 2 fuel oil—not the price of crude oil.

"It's a myth that price differentials between petroleum products are directly related to the price of crude oil," says George Michalski, who conducted the study. "Absolute spreads have remained remarkably constant despite a tenfold range of crude oil prices over the last 20 years."

### How product prices track No. 2 fuel oil*

| Product | Relationship |
|---|---|
| Unleaded regular | 3.5¢/gal over No. 2 fuel oil |
| Unleaded premium | 4¢/gal over unleaded regular |
| Kerosine/Jet A | 3¢/gal over No. 2 fuel oil |
| No. 2 fuel oil | 8% over crude oil |
| No. 6 fuel oil† | 77% of No. 2 fuel oil |
| Bunker fuel§ | 68% of No. 2 fuel oil |

*Based on a 20 year study of price relationships. †0.7% sulfur. §3% sulfur.
Source: Turner, Mason & Co.
OGJ

Once the key No. 2 fuel oil/crude oil price relationship is set, prices of other products can be closely estimated by determining their differentials from No. 2 fuel oil, he says (see table).

The price relationships established in the study represent "equilibrium free market prices prevailing over a reasonable time and can't be used to predict daily spot prices," says Michalski.

**How upgraders performed.** The crude oil price collapse hasn't affected the relative profitability of upgrading processes.

Heavy oil cracking (HOC), a catalytic approach, has continued to outperform coking, a thermal approach, says Chem Systems Inc. (see chart).

That's true even though falling crude oil prices have hurt coker economics less than they have HOC economics, says an official with a major oil company that invested in both types of capacity.

"But offsetting that advantage of the coker is the fact that the fuel consumption of hydroprocessing is much higher, so as prices fall, its fuel costs go down too," he says. "That is, hydrogen and, to some extent, fuel costs are falling in an environment of falling prices."

Factors other than fuel costs have driven some refiners to idle their cokers. Among those factors are an octane shortage, excess fluid catalytic cracking capacity, and a weak coke market.

The manager of one inland coking refinery says he has kept his delayed coker turned off as much as possible this year.

Instead he destroys his resid by charging it to his fluid catalytic crackers, all equipped with high stability, high activity catalysts.

"Coker gasoline is low octane," he says. "And on a liquid basis our coke is worth about $3/bbl. Also, FCC catalysts are much more stable and active than they used to be. Today you can turn up your cat as high as 1,400°F if you want to."

He says that running his coker would have depressed his otherwise high margins.

**HOC benefits.** One of the companies that invested in HOC capacity is Phillips 66 Co., which is running its HOC units at or near capacity.

Richard I. Robinson, vice-president of refining, says Phillips chose the resid desulfurization/HOC route because of the company's refining configuration: it could take advantage of the steam generated and make better use of its hydrofluoric acid alkylation capacity.

Also, Phillips had its own proprietary, bed coil HOC technology.

The HOC units contribute to refinery profitability because their utility costs are down, says Robinson. But the units also earn money for the same reasons they earned money before the crude oil price collapse.

"Our HOC units are contributing to margins because they are upgrading the majority of the barrel into higher value products with little low value coproducts.

"If you produce a higher percentage of the gasoline range products, even in a lower price scenario, those products would still bring the highest price compared to the heavier residual products.

"Even in a period of low prices your light products, meaning anything lighter than resid, are still your most valuable."

**Crude price slump impacts.** The effect of the crude oil price collapse on refiner/marketers has been indirect.

"I don't think the decrease in crude oil prices has had any direct impact on refining or downstream margins," says Diamond's Hemminghaus.

"The result of that decrease, however, has been an increase in demand, and that increase in demand has contributed to higher utilization rates that ultimately should improve profitability."

Marketers credit the decline in gasoline prices with an increased willingness by motorists to buy a higher quality gasoline at less expense than they bought a lower cost, though higher priced, gasoline last year.

That is most clearly seen in the sharp rise in premium unleaded sales (OGJ, July 14, p. 21).

The crude oil price collapse has reduced octane costs, a big help to refiners that are heavy gasoline manufacturers.

Conoco's Dimond says the cost of an octane barrel at the Ponca City refinery has fallen 20-25% from what it was 8-9 months ago.

**Crude supply sources.** The crude oil price collapse has given an advantage to refiners that have not had to buy more remote production because traditional supplies have been shut in.

Some Oklahoma refiners say the decline in the state's production has caused them to have to go to West Texas for intermediate and sour crudes.

One refiner says that around June his transportation costs began rising, and now are up more than $1/bbl from comparable 1985 levels.

Another Oklahoma refiner who noticed a decline in Kansas crude availability around July says his crude acquisition costs have shown a "slight increase."

Not all inland refiners are affected by shut-in production.

Officials at Mapco says their Memphis refinery draws its crude from St. James, La., and they haven't noticed a significant lack of domestic crude availability.

**Capacity cuts helping.** If there is underlying support for refining profits staying strong, it may be due to the fact that industry's most bitter medicine, shutting down refineries, is working.

U.S. operable capacity has remained at or near 15.5 million b/d throughout the year. That contrasts with 18.5 million b/d at yearend 1980.

"I think there is a better balance between demand and supply of refining capacity than what there's been in the past," says a major oil company official.

"A lot of the rationalization has already taken place in the U.S. We're in a position now where any shortfall has to be met by imports."

Major refiners are not the only ones with that view.

"The shutdown of capacity, coupled with an increase in demand, is a significant factor," says Diamond's Hemminghaus. "It has caused the industry to need to run at a utilization rate in the mid-80s."

Significantly, more refinery restarts than closings have been announced in 1986. Since Jan. 1, companies have confirmed plans to restart three refineries with a combined 182,000 b/d of capacity, all on the West Coast.

During the same period, companies announced or accomplished the closures of five plants with a combined 99,900 b/d of capacity, only 26,000 b/d of which is on the West Coast.

Refiners also regard lower crude inventories as a fundamental support for refining profits.

"Margins for industry began turning up in April 1985 when gasoline demand began to pick up," says Hemminghaus. "Refinery runs rose, and industry began to feel the effect of better inventory control."

Besides getting help from reduced capacity and lower crude inventories, U.S. refining margins got some support from lower gasoline inventories.

Total gasoline stocks fell from early July, when refining margins were weakest, until the second half of August, when stocks began rising again. In the first half of September they were below June levels and year earlier levels.

**The outlook.** Margins through November or December will be buoyed by continued strong gasoline demand, say refiner/marketers.

"It's going to taper off, but nevertheless people seem to be doing a lot of driving, as long as gasoline prices stay below a dollar," says a major oil company official.

Another important boost to gasoline margins for the rest of the year is low product inventories.

"Our work has shown a direct correlation between low inventories for products, specifically gasoline, and high refining margins," says William L. Randol of First Boston Corp.

"We'll see firm gasoline pricing through yearend, assuming the Organization of Petroleum Exporting Countries keeps crude prices stable."

Purvin & Gertz Inc. also stresses OPEC's importance to refining profitability.

"A complete failure of OPEC to come up with some form of production control at their early October meeting would...cause prices to decline earlier than had been anticipated," the firm says in its August update.

And that could result in a repeat of the first quarter: refining losses and marketing profits. ▪

## ETHYLENE REPORT

# Ethylene producers may be on verge of better times

## Installed ethylene capacity: 1986

| Company | Location | Capacity, 1,000 metric tons/year | Feed-stock† | Coproducts | Capacity, 1,000 metric tons/year§ |
|---|---|---|---|---|---|
| Allied Corp. (with Borg Warner & BASF-Wyandotte | Geismar, La. | 325 | E,P | Propylene | 21 |
| | | | | Butadiene | 16 |
| Amoco Chemicals Corp. | Chocolate Bayou, Tex. | 975 | E,P,N | Propylene | 390 |
| | | | | Butadiene | 91 |
| | | | | Aromatics | 85 |
| Lyondell Chemical Co. | Channelview, Tex. | 1,270 | E,P,N,G | Propylene | 725 |
| | | | | Butadiene | 200 |
| | | | | Py. gas | 1,180 |
| | | | | Aromatics | 220 |
| | | | | Fuel oils | 670 |
| Corpus Christi Petrochemical Company | Corpus Christi Tex. | 545 | L,H,N,G | Propylene | 256 |
| | | | | $C_4$ | 185 |
| | | | | Benzene | 196 |
| | | | | Py gas | 143 |
| Fina Oil & Chem. | Groves, Tex. | 9 | R | Propylene | 30 |
| Dow Chemical | Freeport, Tex. | 1,136 | E,P,B,N | Propylene | 250 |
| | | | | Butadiene | 39 |
| | Plaquemine, La. | 682 | E,P,B,N | Propylene | 75 |
| Du Pont Petrochemical | Alvin, Tex. | 582 | E,P,B<br>N, G | Propylene | 545 |
| | | | | Aromatics | 522 |
| | Orange, Tex. | 375 | E, P | Propylene | — |
| | | | | $C_4$ | — |
| El Paso Products Co. | Odessa, Tex. | 236 | E,P | Propylene | 65 |
| | | | | Butadiene | 4 |
| | | | | Aromatics | 15 |
| Exxon Chemical U.S.A. | Baton Rouge, La. | 590 | E,P<br>N,G | Propylene | 400 |
| | | | | Butadiene | — |
| | | | | Aromatics | — |
| | Baytown, Tex. | 590 | N,G | Propylene | 408 |
| | | | | Butadiene | 113 |
| B.F. Goodrich | Calvert City, Ky. | 136 | P | Propylene | 90 |
| Chevron Chemical Co. | Port Arthur, Tex. | 432 | LPG | Propylene | 165 |
| | | | | Butadiene | 22 |
| | Baytown, Tex. | 730 | R,N,G | Propylene | 355 |
| | | | | Butadiene | 190 |
| Mobil Chemical Co. | Beaumont, Tex. | 455 | LPG,N | Propylene | 110 |
| | | | | Butadiene | 35 |
| | | | | Aromatics | 35 |
| Northern Petrochemical | Morris, Ill | 430 | E,P,B | Propylene | 110 |
| | | | | Butadiene | 15 |
| | | | | Py gas | 25 |
| | Clinton, Iowa | 365 | E,P | Propylene | 14 |
| | | | | Butadiene | 17 |
| | | | | Py gas | 24 |
| | | | | Fuels | 124 |
| Olin Corp. | Brandenberg, Ky. | 48 | E,LPG | | |
| Phillips Petroleum | Sweeney, Tex. | 1,143 | NGL | Propylene | 170 |
| | | | | Butadiene | 44 |
| Shell Chemical | Deer Park, Tex. | 800 | NGL,R | Propylene | 530 |
| | | | | Butadiene | 50 |
| | | | | Aromatics | 906 |
| | Norco, La. | 1,018 | NGL,R | Propylene | 636 |
| | | | | Butadiene | 227 |
| | | | | Py gas | — |
| Sun-Olin | Claymont, Del. | 109 | R | — | — |
| Texaco | Port Arthur, Tex. | 450 | E,P,N | Propylene | 225 |
| | Port Neches, Tex. | 170 | E,P,R | Propylene | 66 |
| | | | | Butadiene | 227 |
| Texas Eastman | Longview, Tex. | 611 | E,P,N | Propylene | 284 |
| | | | | Aromatics | 101 |
| | | | | Fuel oils | 9 |
| Union Carbide | Seadrift, Tex. | 562 | E,P | Propylene | 46 |
| | | | | Butadiene | — |
| | | | | Aromatics | — |
| | Taft, La. | 500 | LPG,N | Propylene | 193 |
| | | | | Butadiene | — |
| | | | | Aromatics | — |
| | Texas City, Tex. | 702 | LPG,N | Propylene | 136 |
| | | | | Butadiene | — |
| | | | | Aromatics | — |
| U.S.I. | Deer Park, Tex. | 180 | E | — | — |
| USS CHemicals | Houston, Tex. | 227 | NGL,P | Propylene | 75 |
| Vista Chemical Co. | West Lake, La. | 295 | E | Propylene | 8 |
| | | | | Butadiene | 15 |
| | | | | Aromatics | 8 |
| U.S. Total | | 16,778 | | | |

# Installed ethylene capacity: 1986* (continued)

| Company | Location | Capacity, 1,000 metric tons/year | Feed-stock† | Coproducts | Capacity, 1,000 metric tons/year§ |
|---|---|---|---|---|---|
| **ALGERIA** | | | | | |
| Sonatrach | Arzew | 364 | LNG | — | — |
| **ARGENTINA** | | | | | |
| Duperial S.A.I.C. | San Lorenzo | 15 | N | Propylene | 6 |
| | | | | Butadiene | 6 |
| | | | | Py gas | 6 |
| | | | | Fuel oils | 6 |
| Ipako | Ensenada | 15 | R | — | — |
| PASA Petroquimia Arg. | Pto. Gral. San Martin | 23 | P | — | — |
| Petroquimica Bahia Blanca | Bahia Blanca | 200 | E | Propylene | 1 |
| | | | | Butadiene | 10 |
| | | | | Py gas | 7 |
| Argentina total | | 253 | | | |
| **AUSTRALIA** | | | | | |
| Altona Petrochem. Co. Ltd. | Altona, Victoria | 170 | E,G | Propylene | 50 |
| | | | | Butadiene | 17 |
| ICI Australia | Botany, NSW | 250 | N,LPG | Propylene | 95 |
| | | | | Butadiene | 23 |
| | | | | Fuel oils | 16 |
| | | | | Py gas | 70 |
| Australia total | | 420 | | | |
| **AUSTRIA** | | | | | |
| OMV A.G. | Schwechat | 285 | B,N,G | Propylene | 150 |
| | | | | Butadiene | 50 |
| | | | | Py gas | 230 |
| **BELGIUM** | | | | | |
| Petrochem S.A. | Antwerp | 502 | N | Propylene | 230 |
| | | | | Butadiene | 65 |
| | | | | Aromatics | 230 |
| | | | | Fuel oils | 85 |
| | | | | Py gas | 150 |
| **BOLIVIA** | | | | | |
| Yacimientos Petroliferos Bolivianos | La Paz | 230 | E,P | Propylene | 56 |
| | | | | Py gas | 22 |
| **BRAZIL** | | | | | |
| Brasiliera de Estireno | Sao Paulo | 5 | EtOH | — | — |
| Industrias Quimicas Electro Cloro | Elclor | 11 | EtOH | — | — |
| Copene Petroquimica | Camaracari-Bahia | 460 | N,G | Propylene | 243 |
| | | | | Butadiene | 55 |
| | | | | Py gas | 341 |
| | | | | Aromatics | 163 |
| | | | | Fuel oils | 92 |
| Copesul | Triunfo RGS | 420 | N | Propylene | 227 |
| | | | | Butadiene | 66 |
| | | | | Py gas | 192 |
| | | | | Aromatics | 176 |
| | | | | Fuel oils | 80 |
| Coperbo | Cabo | 32 | EtOH | — | — |
| Petroquimica Uniao S.A. | Santo Andre | 360 | N | Propylene | 204 |
| | | | | Py gas | 103 |
| | | | | Butadiene | 50 |
| | | | | Aromatics | 312 |
| Salgema Industrias Quimicas S.A. | Maceio-Alagoas | 100 | EtOH | — | — |
| Union Carbide | Cubatao | 40 | EtOH | — | — |
| Brazil total | | 1,428 | | | |
| **CANADA** | | | | | |
| Alberta Gas Ethylene | Joffre, Alta. | 1,224 | | Propylene | 35 |
| | | | | Butadiene | 51 |
| | | | | Py gas | 34 |
| Dow Chemical | Sarnia, Ont. | 50 | P,B,R | Propylene | — |
| Imperial(Essc Chemical) | Sarnia, Ont. | 220 | NGL | Propylene | 40 |
| | | | | Butadiene | 8 |
| | | | | Py gas | 25 |
| Petromont | Varnenes, Que. | 225 | N | Propylene | — |
| | Montreal East | 68 | P,R | Propylene | 60 |
| | | | | Butadiene | 2 |
| | | | | Py gas | 2 |
| | | | | Aromatics | 6 |
| Polysar Ltd. | Corunna (Sarnia), Ont. | 455 | E,N,G | Propylene | 330 |
| | | | | Butadiene | 91 |
| | | | | Aromatics | 125 |
| Canada total | | 2,242 | | | |
| **CHILE** | | | | | |
| Empressa Nacional Del Petr. | Talcahuano | 60 | N | — | — |
| **COLOMBIA** | | | | | |
| Empresa Colombiana | Barrancabermeja | 115 | E,R | Propylene | 6 |
| | | | | Py gas | 5 |
| **FINLAND** | | | | | |
| Neste Oy | Porvoo | 200 | N,G, R,NGL | Propylene | 30 |
| | | | | Butadiene | 20 |
| **FRANCE** | | | | | |
| Atochem & Chloe Chimie | Lacq, Gonfreville, & Feyzin | 830 | E,N | Propylene | 390 |
| | | | | Butadiene | 155 |
| | | | | Aromatics | 330 |
| | Carling St. Avoid | 440 | N,G | Propylene | 220 |
| | | | | $C_4$ | 140 |
| | | | | Py gas | 420 |
| | | | | Aromatics | 150 |
| | | | | Fuel oils | 80 |
| Copenor | Dunkerque | 225 | N,G,LPG | Propylene | 110 |
| | | | | $C_4$ | 75 |
| | | | | Py gas | 70 |
| | | | | Aromatics | 80 |
| | | | | Fuel oils | 50 |
| Napthachimie | Lavera | 240 | LPG,N | Propylene | 155 |
| | | | | Butadiene | 50 |
| Shell Chimie | Berre | 380 | N,G,LH | Propylene | 190 |
| | | | | Butadiene | 75 |
| Esso Chimie | Notre Dame de Gravenchon | 300 | N,R | Propylene | 220 |
| | | | | Butadiene | 70 |
| | | | | Py gas | 310 |
| France total | | 2,415 | | | |
| **GERMANY** | | | | | |
| BASF A.G. | Ludwigshafen | 450 | N | Propylene | 240 |
| | | | | $C_4$ | 220 |
| | | | | Py gas | 264 |
| Deutsche Marathon | Burghausen | 200 | E,P,N | Propylene | 140 |
| | | | | Butadiene | 84 |
| | | | | Benzene | 124 |
| Deutsche Texaco A.G. | Heide | 80 | N | Propylene | 55 |
| | | | | $C_4$ | 28 |
| Erdolchemie G.m.b.H. | Worringen | 740 | N | Propylene | 520 |
| | | | | Butadiene | 245 |
| | | | | Aromatics | 200 |
| Esso Chemie G.m.b.H. | Cologne | 450 | N | Propylene | 240 |
| | | | | $C_4$ | 38 |
| Rheinische Olefin-werke | Wesseling | 650 | N,G | Propylene | 300 |
| | | | | Butadiene | 150 |
| | | | | Py gas | 520 |
| Union Rheinische Braun-Kohlen Krafstoff A.G. | Wesseling | 440 | N | Propylene | 260 |
| | | | | $C_4$ | 150 |
| | | | | Py gas | 595 |
| | | | | Fuel oils | 165 |
| Ruhr Oel A.G. | Gelsenkirchen | 400 | N | Propylene | 245 |
| Verba Oel | Munchsmunster | 200 | N | Propylene | 130 |
| Chemische Werke Huls | Marl | 50 | LPG | — | — |
| Germany total | | 3,660 | | | |
| **GREECE** | | | | | |
| EKO Chemicals Co. | Thessaloniki | 15 | N | — | — |
| **INDIA** | | | | | |
| Alkali & Chemical Corp. | Rishra, W. Bengal | 12 | EtOH | — | — |
| Chemicals & Plastics India | Krishnagiri | 19 | EtOH | — | — |
| McDowell & Co. | Visakhapatnam | 3 | EtOH | — | — |
| India Petrochem Corp. | Baroda | 130 | N | Propylene | 81 |
| | | | | Butadiene | 22 |
| | | | | Benzene | 24 |
| | | | | Py gas | 29 |
| | | | | Aromatics | 20 |
| National Organic Chemicals Industries Ltd. | Thana, Bombay | 63 | N | Propylene | 37 |
| | | | | Butadiene | 7 |
| Polychem Ltd. | Bombay | 2 | EtOH | — | — |
| | Nira | 4 | EtOH | — | — |
| Reliance Textile Ind. | Bombay | 22 | N | Propylene | 6 |
| | | | | Benzene | 3 |
| | | | | Aromatics | 6 |
| | | | | Fuel oils | 6 |
| India total | | 252 | | | |
| **IRAN** | | | | | |
| Abadan Petrochemical | Abadan | 26 | R | Propylene | 15 |
| **ISRAEL** | | | | | |
| Oil Ref. Ltd. | Haifa | 130 | N,R,LPG | — | — |

# Installed ethylene capacity: 1986* (continued)

| Company | Location | Capacity, 1,000 metric tons/year | Feed-stock† | Coproducts | Capacity, 1,000 metric tons/year§ |
|---|---|---|---|---|---|
| **ITALY** | | | | | |
| Enichem | Gela | 200 | E,N | Propylene | 160 |
| | | | | Butadiene | 40 |
| | | | | Py gas | 280 |
| | | | | Aromatics | 150 |
| | | | | Fuel oils | 55 |
| | Priolo | 215 | N | Propylene | 150 |
| | Brindisi | 130 | N | Propylene | 85 |
| | | | | Butadiene | 120 |
| | Porto Tores | 240 | N | Propylene | 121 |
| | | | | Butadiene | 50 |
| ICAM | Priolo | 550 | N,G | Propylene | 350 |
| Montedipe | Porto Marghera | 350 | N | Propylene | 180 |
| Italy total | | 1,485 | | | |
| **JAPAN** | | | | | |
| Idemitsu Petrochem Co. Inc. | Tokuyama | 380 | N | Propylene | 220 |
| Maruzen Petrochem Co. Inc. | Goi | 373 | N | Propylene | 220 |
| | | | | Butadiene | 55 |
| | | | | Aromatics | 240 |
| Mitsubishi Chemical Industries | Mizushima | 360 | N,LPG | Propylene | 216 |
| Mitsubishi Petrochemical Co. Inc. | Kashima | 299 | N | — | — |
| | Yokkaichi | 211 | N | — | — |
| Mitsui Petrochemical Inds. | Chiba | 140 | N | Propylene | 68 |
| | | | | Py gas | 90 |
| | | | | Fuel oils | 30 |
| | Iwakuni-Ohtake | 92 | N | Propylene | 69 |
| | | | | Py gas | 64 |
| Mizushima-Ethylene | Mizushima | 360 | N,LPG | Propylene | 216 |
| | | | | Py gas | 250 |
| | | | | Fuel oils | 50 |
| Nippon Petrochemicals | Kawasaki | 190 | N,LPG | Propylene | 148 |
| | | | | Butadiene | 50 |
| Osaka Petrochemicals Inds. | Osaka | 300 | N,B | Propylene | 200 |
| | | | | Aromatics | 225 |
| Sanyo Ethylene Co. | Mizushima | 390 | N | Propylene | 254 |
| Shin Daikyowa Petrochemical Co. | Yokkaichi | 361 | N,B,P | Propylene | 220 |
| | | | | Py gas | 300 |
| | | | | Aromatics | 169 |
| Showa Denko, K.K. | Ohita | 320 | N,LPG | Propylene | 170 |
| | | | | Butadiene | 45 |
| | | | | Aromatics | 160 |
| Sumitomo Chem. Co. Ltd. | Chiba | 345 | N,LPG | Propylene | 259 |
| | Nihama | 139 | N | Propylene | 123 |
| Tonen Petrochemical Co., Ltd. | Kawasaki | 350 | N,LPG | Propylene | 224 |
| | | | | Butadiene | 105 |
| Ukishima Petrochem Co. Ltd. | Kawasaki | 808 | N | Propylene | 417 |
| Japan total | | 5,418 | | | |
| **KOREA** | | | | | |
| Honam Ethylene Co. | Yeochun | 350 | N,G,LPG | Propylene | 187 |
| | | | | $C_4$ | 129 |
| | | | | Aromatics | 155 |
| | | | | Py gas | 302 |
| | | | | Fuel oils | 98 |
| Yukong Ltd. (formerly Korea Oil) | Ulsan | 155 | N | Propylene | 81 |
| | | | | Butadiene | 24 |
| | | | | Aromatics | 70 |
| | | | | Fuel oils | 18 |
| Korea total | | 505 | | | |
| **MEXICO** | | | | | |
| Petroleos Mexicanos | Congrejera | 500 | | | |
| | Pajaritos | 209 | E | | |
| | Posa Rica | 182 | R | | |
| | Reynosa | 27 | LH | | |
| | Ciudad Madero | 14 | R | | |
| Mexico total | | 932 | | | |
| **THE NETHERLANDS** | | | | | |
| Dow Chemical Europe | Terneuzan | 960 | N | Propylene | 450 |
| | | | | Benzene | 600 |
| | | | | Butadiene | 150 |
| DSM | Limburg | 800 | N,G,LPG | Propylene | 450 |
| | | | | Benzene | 150 |
| | | | | Butadiene | 90 |
| Shell Nederland Chemie BV | Moerdijk | 500 | N,G | Propylene | 300 |
| | | | | Butadiene | 115 |
| Netherlands total | | 2,260 | | | |
| **NORWAY** | | | | | |
| I/S Noretyl | Rafnes | 300 | NGL | Propylene | 70 |
| | | | | Py gas | 35 |
| **PORTUGAL** | | | | | |
| Companhia Nacional de Petroquimica | Sines | 300 | LPG,N | Propylene | 140 |
| | | | | Butadiene | 42 |
| | | | | Py gas | 220 |
| | | | | Fuel oils | 24 |
| **PUERTO RICO** | | | | | |
| Union Carbide Caribe Inc. | Ponce | 413 | N,LPG | Propylene | 227 |
| **QATAR** | | | | | |
| Qatar Petrochemical | Umm Said | 280 | E | Propylene | 5 |
| **SAUDI ARABIA** | | | | | |
| Saudi Petrochemical Co. | Al-Jubail | 656 | E | — | — |
| Arabian Petrochemical Co. | Al-Jubail | 500 | E | — | — |
| Saudi Yanbu Petrochem. Co. | Yanbu | 455 | E | — | — |
| Saudi Arabia total | | 1,611 | | | |
| **SINGAPORE** | | | | | |
| Singapore Petro-Chemical | Singapore | 300 | LPG,N | Propylene | — |
| **SOUTH AFRICA** | | | | | |
| So. Africa Coal, Oil & Gas Co. | Sasolburg | 150 | Syn. gas | Propylene | 120 |
| | | | | Butadiene | 27 |
| | | | | Aromatics | 20 |
| **SPAIN** | | | | | |
| Dow | Tarragona | 350 | N | Propylene | 130 |
| | | | | Butadiene | 50 |
| | | | | Py gas | 300 |
| Enpetrol | Puertollano | 210 | LPG,N,G | Propylene | 115 |
| | | | | Butadiene | 28 |
| | | | | Py gas | 155 |
| | | | | Fuel oils | 45 |
| | Tarragona | 325 | LPG,N | Propylene | 150 |
| | | | | Butadiene | 45 |
| | | | | Py gas | 260 |
| | | | | Fuel oils | 70 |
| Industrias Quimicas Asociadas S.A. | Tarragona | 71 | N | Propylene | 36 |
| | | | | Butadiene | 7.5 |
| | | | | Aromatics | 40 |
| Spain Total | | 956 | | | |
| **SWEDEN** | | | | | |
| Statoil Petrochemie A/B | Stenungsund | 365 | LPG,N,G | Propylene | 165 |
| **SWITZERLAND** | | | | | |
| Lonza, A.G. | Visp | 30 | N,LPG | Acetylene | |
| **TAIWAN** | | | | | |
| Chinese Petro. Corp. | Koahsiung | 899 | N | Propylene | 469 |
| | | | | Butadiene | 128 |
| China Petrochemical Development Corp. | Toufen | 54 | E | — | — |
| Taiwan total | | 953 | | | |
| **TURKEY** | | | | | |
| Petkim Petrokimya A.S. | Izmit | 55 | N | Propylene | 40 |
| | | | | $C_4$ | 26 |
| | | | | Py gas | 58 |
| | | | | Fuel oils | 8 |
| | Izmir | 300 | N | Propylene | 88 |
| | | | | $C_4$ | 80 |
| | | | | Py gas | 250 |
| Turkey total | | 355 | | | |
| **UNITED KINGDOM** | | | | | |
| BP Chemicals | Baglan Bay | 340 | N | Propylene | 200 |
| | | | | Butadiene | 60 |
| | Grangemouth | 250 | | Propylene | 180 |
| | | | | Butadiene | 48 |
| BP/ICI | Wilton | 650 | N | Propylene | 300 |
| | | | | Butadiene | 80 |
| Essochem Olefins Inc. | Fawley | 105 | N,G | Propylene | 100 |
| | | | | Butadiene | 80 |
| | Fife | 500 | E | | |
| Shell Chemicals U.K. Ltd. | Carrington | 150 | N,G,LPG | Propylene | 90 |
| | | | | Butadiene | 30 |
| U.K. total | | 1,995 | | | |
| **VENEZUELA** | | | | | |
| Pequiven | El Tablazo | 150 | E,P | Propylene | 45 |
| | | | | Aromatics | 13 |
| **WORLD TOTAL** | | **48,151** | | | |

*(As of June 1, 1986)

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†Key: E = ethane, P = propane, B = butane, R = refinery streams, N = naphtha, G = gas oil, LH = light hydrocarbons, NGL = natural gas liquids (ethane, propane, butane), LPG = liquefied petroleum gas (propane, butane), EtOH = ethanol

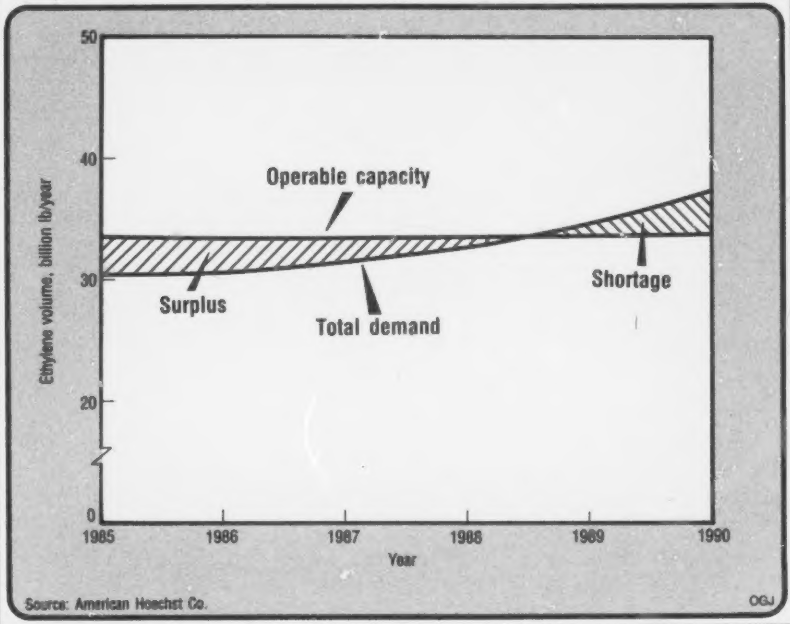
§Coproduct production is only estimated or design quantity. Actual production can vary widely depending on feedstock slate, severity, etc.

# Ethylene capacity by country

| Area | 1,000 metric tons/year<br>1984 | <br>1985 | <br>1986 |
|---|---|---|---|
| North America | | | |
| U.S. | 17,073 | 17,298 | 16,778 |
| Canada | 1,561 | 2,242 | 2,242 |
| **Total** | **18,634** | **19,540** | **19,020** |
| Latin America | | | |
| Argentina | 253 | 253 | 253 |
| Bolivia | 230 | 230 | 230 |
| Brazil | 1,407 | 1,427 | 1,428 |
| Chile | 60 | 60 | 60 |
| Colombia | 115 | 115 | 115 |
| Mexico | 932 | 932 | 932 |
| Puerto Rico | 413 | 413 | 413 |
| Venezuela | 150 | 150 | 150 |
| **Total** | **3,560** | **3,580** | **3,581** |
| Western Europe | | | |
| Austria | 265 | 285 | 285 |
| Belgium | 520 | 520 | 520 |
| Finland | 200 | 200 | 200 |
| France | 2,270 | 2,270 | 2,415 |
| West Germany | 3,990 | 3,990 | 3,660 |
| Greece | 15 | 15 | 15 |
| Italy | 1,485 | 1,485 | 1,485 |
| The Netherlands | 2,260 | 2,260 | 2,260 |
| Norway | 300 | 300 | 300 |
| Portugal | 300 | 300 | 300 |
| Spain | 956 | 956 | 956 |
| Sweden | 350 | 360 | 365 |
| Switzerland | 30 | 30 | 30 |
| U.K. | 2,270 | 2,270 | 1,995 |
| **Total** | **15,261** | **15,291** | **14,786** |
| Asia/Pacific | | | |
| Australia | 420 | 420 | 420 |
| India | 252 | 252 | 252 |
| Japan | 5,995 | 5,581 | 5,418 |
| Korea | 505 | 505 | 505 |
| Singapore | 300 | 300 | 300 |
| Taiwan | 955 | 953 | 953 |
| **Total** | **8,428** | **8,011** | **7,848** |
| Other | | | |
| Algeria | 120 | 120 | 364 |
| Iran | 26 | 26 | 26 |
| Israel | 24 | 24 | 130 |
| Qatar | 280 | 280 | 280 |
| Saudi Arabia | — | 1,611 | 1,611 |
| South Africa | 150 | 150 | 150 |
| Turkey | 355 | 355 | 355 |
| **Total** | **655** | **2,566** | **2,916** |
| **World total** | **46,538** | **48,988** | **48,151** |

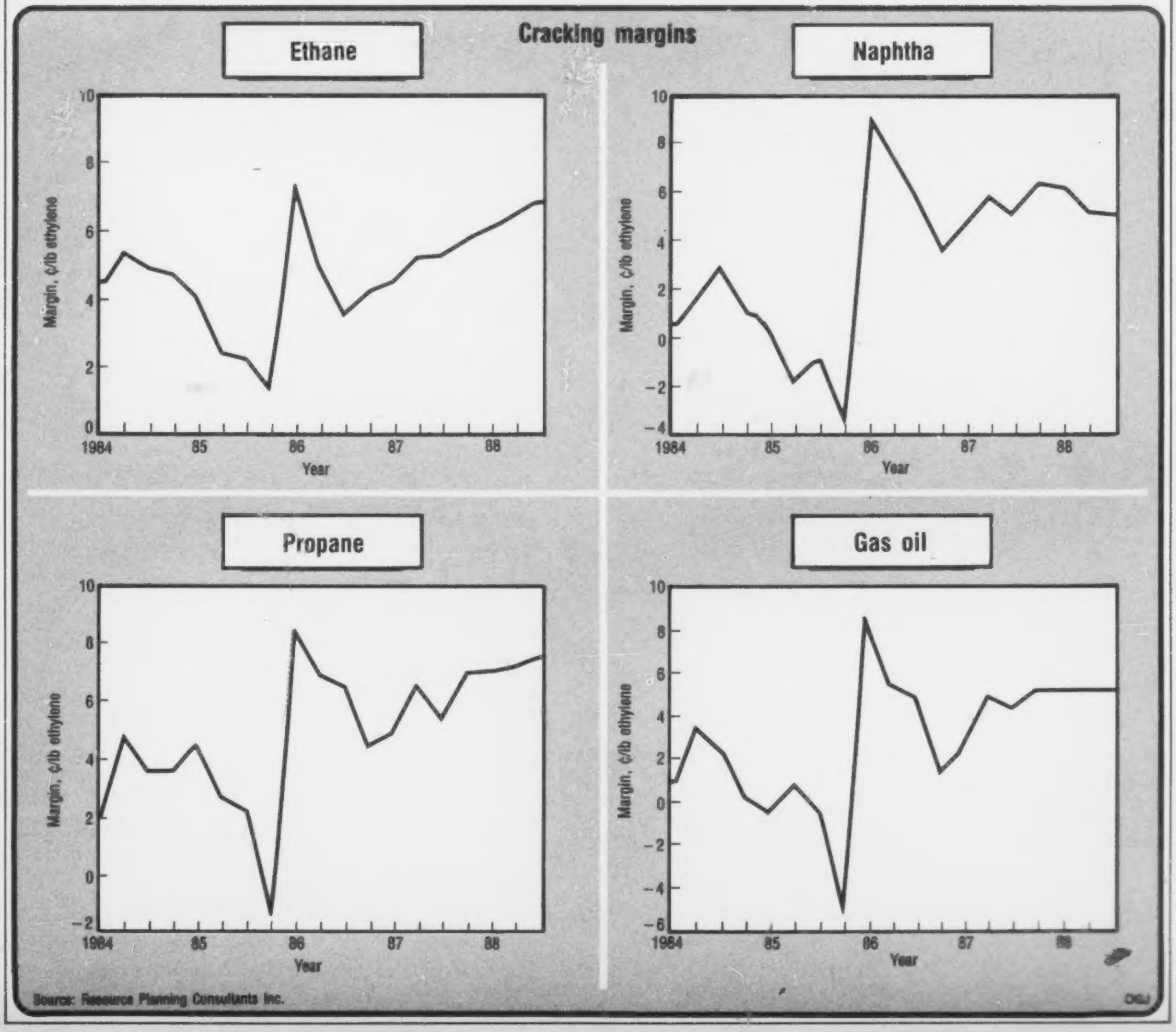
*As of June 1, 1986.

## Ethylene shortage may appear in 1988



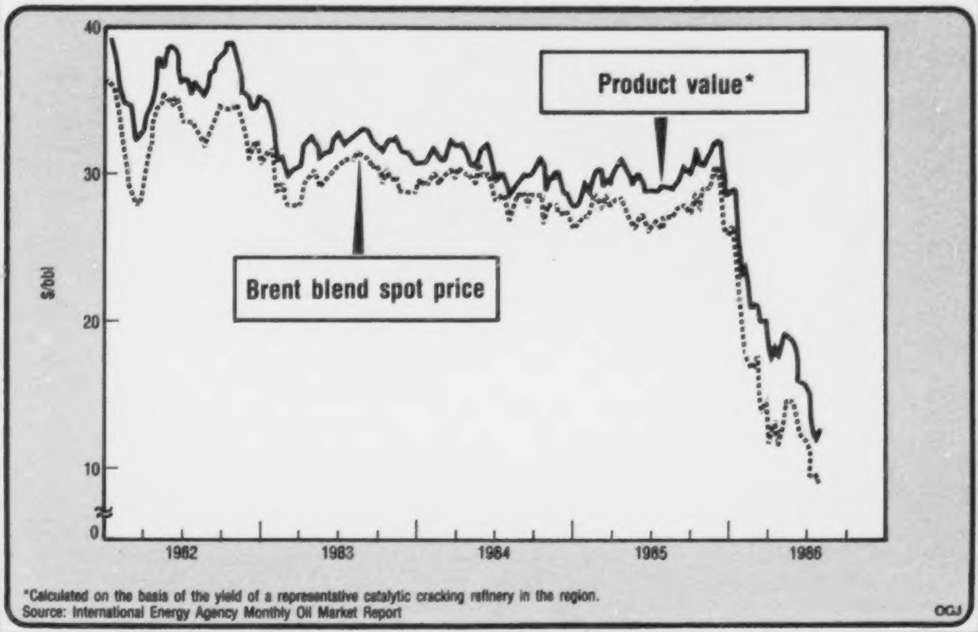
Source: American Hoechst Co.

## Low oil prices depress ethane's feedstock value



Source: Resource Planning Consultants Inc.

How market prices plunged in western Europe



*Calculated on the basis of the yield of a representative catalytic cracking refinery in the region.
Source: International Energy Agency Monthly Oil Market Report

# Rapid decline in crude oil prices buoys profits for refiners in western Europe

**Roger Vielvoye,** International Editor

Europe's refining industry has completed its most profitable 6 months in 20 years.

Downstream earnings helped integrated companies offset a sharp drop in the normally more generous upstream margins.

But prospects for maintaining healthy downstream returns for the rest of the year are uncertain. Rising crude oil prices and a growing surplus of products, generated by netback crude pricing, threaten to trigger a new outbreak of downstream competition that could reduce returns considerably.

Product prices that lagged spectacular declines in crude oil prices played a major part in running up generous downstream margins during first half 1986.

Figures compiled by the International Energy Agency peg North Sea Brent blend crude oil spot price at $9/bbl and Brent blend product values in Northwest Europe at $12.36/bbl last month.

The crude price was down 66% and product value down 57% from last December. The crude price slumped past the $20/bbl mark in January and the $15/bbl mark in March. But product values didn't drop past the same marks until

March and July.

All figures are for the end of the month.

North Sea Brent blend run through an upgraded refinery produced an average profit of $4.70/bbl for European refiners in the second quarter, compared with $3.90/bbl in the first quarter.

Figures from London brokers Scrimgeour Vickers & Co. show that on the same basis netbacked Arabian light produced a second quarter margin of $2.64/bbl vs. only 61¢/bbl in the first quarter.

The crude oil price recovery after the most recent meeting of the Organization of Petroleum Exporting Countries in Geneva has eaten into refiners' margins.

However, the European refining industry is basically sound. Most of the major refinery closures have been completed or are in progress, and the considerable surplus capacity that remains may not have a significant international effect.

Integrated oil companies that have been through the trauma of contraction and restructuring seem determined to hang onto some of the margins they earned in the first half of the year.

It is a policy determined by necessity. Companies that previously subsidized losses in refining and marketing from upstream profits no longer have that option.

Ultimately, however, refiners' policies on handling netback crude will determine whether downstream operations remain a profit-making sector, able to compensate for some upstream reverses.

Netback pricing of most OPEC crudes, which guarantees refiners a margin, has encouraged crude oil runs that cannot be justified by the current product market. As a result, products stocks are growing, and there are signs that this could once again unleash a round of savage retail price cutting.

Refiners take an ambivalent attitude toward netbacks. They like the margins but do not relish the effects of overproduction.

The future of netbacks will be discussed when OPEC ministers meet again in October. But, as one company executive said, it is difficult to see netbacks being phased out.

Without them OPEC would be forced to tackle the problem of differentials. It is unlikely that members will want to do that with so many other problems confronting them.

**Downstream turnaround.** Even before the start of the crude oil price collapse in January, European downstream operations, particularly refining, were beginning to operate at a profit. The whole downstream sector started to turn around in the third quarter of 1985. And in the last 3 months of the year margins reached acceptable levels—even at a crude oil price of $28-30/bbl.

During the past decade European refining was plagued by declining products demand that produced a massive surplus of distillation capacity.

Marketing suffered from the pursuit of volume in a contracting business that produced enormous competitive pressures and poor financial returns.

During this period downstream operations were a financial millstone around the necks of integrated companies. The downstream segment built up multibillion dollar losses. And since crude oil prices started to fall it also has experienced big inventory losses.

All European refiner/marketers are about in the same position, said one company executive, and they need today's improved margins to offset yesterday's stock losses.

When stock losses are under control there will be a greater temptation to take advantage of the competitive situation emerging in the marketplace.

**A boost for refining.** The turnaround in the refining sector occurred when demand was growing slowly. For the first time refiners reaped the benefits of industry's refinery closure program and huge investments in upgrading.

During the previous 5 years 150 million tons/year of capacity was taken out of commission. A large part of this shutdown occurred in 1983-85.

Refiners also were helped by the declining value of the dollar throughout 1985 and its continuing weakness in the first half of this year.

Kent Bowden, vice-president of Conoco Inc.'s European refining and marketing, said margins for the first half of the year were "the best in my memory."

He said, "But those high margins are just about gone, and they are not going to pop back into our laps."

In Britain, Conoco's biggest market, the company was recently selling products substantially below cost until it pushed through a gasoline price increase.

Conoco is one of the most aggressive gasoline marketers in Europe. It has just started up a 35,000 b/d cat cracker at its Humber, U.K., refinery, acknowleged to be among the most profitable processing units in Europe.

Bowden said increased margins mean that a little more money is available for investment.

Much of it will be spent on "doing things we have not had the cash to do in the past few years." This includes service station improvements and image building programs.

The company, which recently acquired new gasoline outlets in West Germany, Holland, and Denmark, will continue to look for new business opportunities.

But Bowden reflects the general attitude of the downstream side of the business when he says Conoco is not expanding for the sake of expansion.

"We are looking for ways to make more money efficiently," he said.

**Unleaded, sulfur content.** Improved margins coincided with heavy investments by most refiners in preparation for introduction of unleaded gasoline throughout Europe in mid-1989. Unleaded gasoline is currently available only from selected outlets.

Industry sources estimate it will cost $2.6-2.9 billion to produce unleaded gasoline in large volumes. Most of the spending will go into reforming plants.

Refiners also face the prospect of a reduction in the sulfur content of gas oils to 0.3 wt % with a 0.2 wt % limit in some regions. A proposal for the reduction has been put to the European Community (EC), but so far there has been no agreement.

Companies are concerned that adoption of the 0.2 wt % limit in some regions will require additional investment. They also point out that the tax regime in some countries is boosting demand for diesel powered vehicles at the expense of gasoline.

If the trend continues there might be difficulties in maintaining diesel fuel quality, especially cetane numbers and fuel density.

All companies are watching closely for the effect of lower prices on longer term demand. So far there has been little cause to expect increased consumption based on prices.

There was a spring gas oil boom in West Germany, but that was caused by customers taking advantage of low prices and stocking up for next winter 5-6 months early.

Residual fuel oil has made very limited progress in part of the West German and Italian steel, cement, and power generating markets. Only dual fired capacity has switched to oil mainly from coal, and those units are expected to switch back to coal when fuel oil prices start to harden.

The most optimistic forecasts see a slowing in the sharp decline in the use of resid in Europe.

**Refinery closures.** Among larger refiner/marketers there is a general feeling that the bulk of the refinery closure program in Europe may be over.

All units with high quality upgrading are working at more than 80% of capacity, and many are running at full tilt.

Surplus refining capacity is almost exclusively confined to basic processing units, although closures have not been confined to this type of unit. Older capacity with a range of upgrading has been shut down in Britain and West Germany.

High throughput at upgraded refineries is largely responsible for the more healthy base for European refining. After the U.K. miners' strike, which boosted residual fuel oil demand by as much as 400,000 b/d, the barrel whitened and profits went up.

Conoco's Bowden is among major company officials who believe the majority of plant closures in Europe is over. There is still some surplus capacity, he said, but that will always be true.

That is a view reflected by Robert O. Swanson, Mobil Oil Corp.'s executive vice-president of international marketing and refining.

Mobil, with one of industry's more aggressive closure policies, has shut down 45% of its European capacity.

Refineries in Holland, Germany, and Italy have been closed, and the company is in the process of closing a unit in France. Remaining units are working at 90% of capacity and on the edge of 100% for upgrading.

Two refineries in Antwerp, Belgium, and one in Trieste, Italy, have been bought by independents intent on taking advantage of improved economics in European refining. Reports that other units were to be acquired proved groundless, and industry sources said rising crude prices and the prospect of lower margins may kill any plans that have not come to fruition.

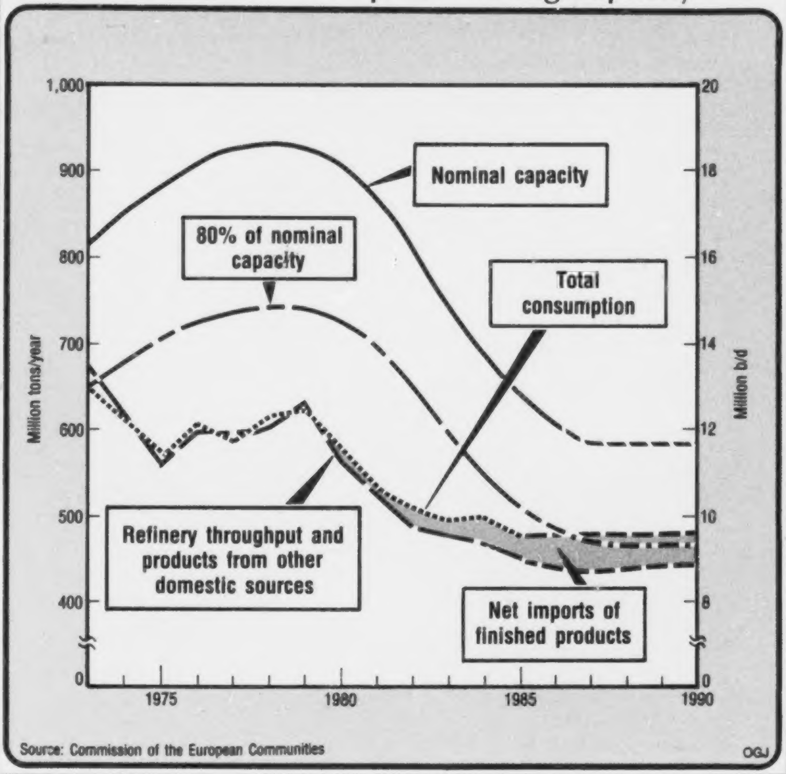
**Where the shutdowns are.** EC figures show that at the end of 1985 primary distillation capacity in the 12 member countries stood at 615 million tons/year. That was 50 million tons/year more than was required to produce a utilization factor of 80%. Closures wiped out 40 million tons/year of capacity during 1985.

The surpluses are for EC as a whole and do not reflect progress made toward bringing the system into balance in countries like Britain, West Germany, and Denmark, where utilization rates are more than 80%.

Other EC members are France, Italy, Netherlands, Belgium, Luxembourg, Ireland, Greece, Spain, and Portugal. Only Luxembourg has no refining capacity.

In West Germany, four refineries with a combined capacity of 16 million tons/year were closed during 1985, reducing total capacity to 88.1 million tons.

The decline in W. Europe's refining capacity



Source: Commission of the European Communities

A further 7.8 million tons of closures were planned for this year, although this could be reduced to only 2.3 million tons if Esso AG sells its Hamburg, W. Germany, refinery to Coastal Corp., Houston.

British refining capacity fell to 87.6 million tons/year from 99.1 million tons last year. No further plant closures are planned. Minor reductions in capacity at existing plants will trim capacity to 85.8 million tons/year by the end of the decade.

In countries like Italy and Portugal utilization is only 60%. In Italy in particular the limited closure program has barely dented surplus refining capacity.

Two refineries with a combined capacity of 6.5 million tons/year were shut down last year in Italy. Cutbacks at existing units are to remove 2.5 million tons this year. One more plant closure is scheduled during the next 2 years, along with a 3.3 million ton reduction in capacity at operating units.

That will leave Italy with an inflated 11.7 million tons/year of distillation capacity by the turn of the decade.

France is starting to make inroads into its big surplus. Capacity was unchanged last year. But this year Shell and Mobil will shut down big units, while distillation towers will close in operating plants.

The 1986 closure program is scheduled to reduce French capacity to 96.8 million tons/year.

EC says planned closures in France and Italy will reduce primary distillation capacity in member states to 575 million tons/year by 1990.

While French refiners were helped by the fall in crude oil prices, dollar depreciation, and restructuring, assistance also came from the lifting of all remaining price controls on oil products.

In the first half of the year the French refining industry made $886 million, its first profit since 1974. Stock losses cost $2.6 billion.

Between 1974 and 1985 French refiners chalked up losses of $11.8 billion and debts of $11 billion.

Oil companies hope a wave of liberalization that has been sweeping the country since the right wing government came to power in March will remove remaining constraints under the 1928 law that governs the oil industry. There is even hope that the law might be scrapped completely.

The law, which gives the state a monopoly over oil imports and refining in France, originally was designed to build a powerful refining industry. The state delegates the monopoly to

Cie. Franaise des Petroles, Ste. Nationale Elf Aquitaine, Esso SAF, BP, Shell France, and Mobil France, subject to a number of conditions that companies say are responsible for a large share of their losses during the past 15 years.

Once a pampered industry, refining became the main target of a national energy policy designed to reduce oil's share in the French energy mix.

This policy built a massive nuclear program, which currently supplies 65% of France's electricity. Nuclear power reduced France's heavy fuel oil consumption to 8.6 million tons last year from 36.2 million tons in 1973.

With removal of price controls, French refiners are able to adapt quickly to international market prices, something they were prevented from doing before.

They also hope the new government will lift or reduce the tax on heavy fuel oil, which was doubled earlier this year as oil prices fell.

Other measures French refiners want scrapped are a requirement to carry two thirds of imported crude and products in French flag tankers and an obligation to refine in France or the EC 90% of products sold on the French market.

Although the obligation is not a great handicap, French refiners note that a requirement for independent marketers to buy 80% of their products from French or European refiners has been lifted.

If all constraints and discriminations were lifted, the industry thinks French oil consumption would stabilize at about the 80 million ton figure achieved last year, and no further refinery closures would be needed.

The other market in Europe where major structural downstream changes are in progress is Spain.

As a result of entry into the EC at the beginning of this year, the Spanish government has a 6 year transitional period to break up state owned Campsa's distribution monopoly. In preparation for loss of this monopoly, Campsa is investing $850 million to streamline its operations. This will involve the loss of more than 2,000 jobs.

Spain also has seen a growing foreign interest in its refining industry. Petroleos Mexicanos SA holds a 34.28% interest in Spain's Petroleos del Norte, while Petroleos de Venezuela SA is believed to have acquired a 5% stake in Petroleos del Mediterraneo SA, probably Spain's most profitable refining operation, through a U.S. investment group.

Abu Dhabi's International Petroleum Investment Co. is acquiring a 20% interest in Cia. Espanola de Petroleos SA. •

# Isomerization, blending, key octane sources at refinery

**REFINING REPORT**

**James W. Jones**
La Gloria Oil & Gas Co.
Tyler, Tex.

To cope successfully with the Environmental Protection Agency (EPA) mandated tetra-ethyl lead (TEL) phasedown, La Gloria Oil & Gas Co., a wholly owned subsidiary of Texas Eastern Corp., is pursuing several alternatives for increasing its gasoline pool octane at its Tyler, Tex., refinery.

Among the alternatives, once-through isomerization, lead banking, and a new blending facility are important and successful sources of additional octane.

The 46,000-b/d fuels refinery is the center of La Gloria's manufacturing activities. It supplies the majority of fuel products marketed by the company in East Texas and the Midwest. It is a full-conversion facility with ample catalytic cracking, coking, reforming, and alkylation capacity. As a result, the refinery was able to meet the 0.5 g/gal TEL limit imposed by EPA on July 1, 1985.

The refinery has developed several programs to ensure capability to meet the 0.1 g/gal limit imposed Jan. 1, 1986, as well as the eventual ban of TEL. These plans include taking advantage of the opportunity of the EPA "banking" rules, utilizing octane-enhancing FCC catalysts, test marketing Oxinol-gasoline blends, and revamping an idle fixed-bed catalytic reformer to an isomerization unit.

Plans are also being developed to meet potential octane needs beyond the capability of these programs, ensuring La Gloria's ability to respond to a presently uncertain gasoline market.

La Gloria's first step in preparation for the total phaseout of TEL was made in 1977 when the refinery was expanded to its present capability. Along with energy conservation, environmental compliance, and increased throughput, the manufacturing of 100% unleaded gasoline was a prime consideration of the expansion.

Naphtha hydrodesulfurization (HDS) capacity was increased to provide processing for all heavy naphtha as reformer feed, as well as the treating of all light naphtha as potential isomerization feed. The refinery now has naphtha HDS capacity equal to 40% of crude capacity.

Reforming capacity was also increased to allow processing of all heavy naphtha, some of which previously had to be blended into leaded gasoline, and now represents 30% of crude charge. Overall reformer, octane capability was increased as well.

A 12,000-b/d continuous catalytic regeneration (CCR) Platformer, designed for 100+ research octane (RON) clear, was installed, representing 80% of the refinery's reforming capacity.

This unit enabled the refinery to

Fig. 1

Tyler refinery rack-blending system

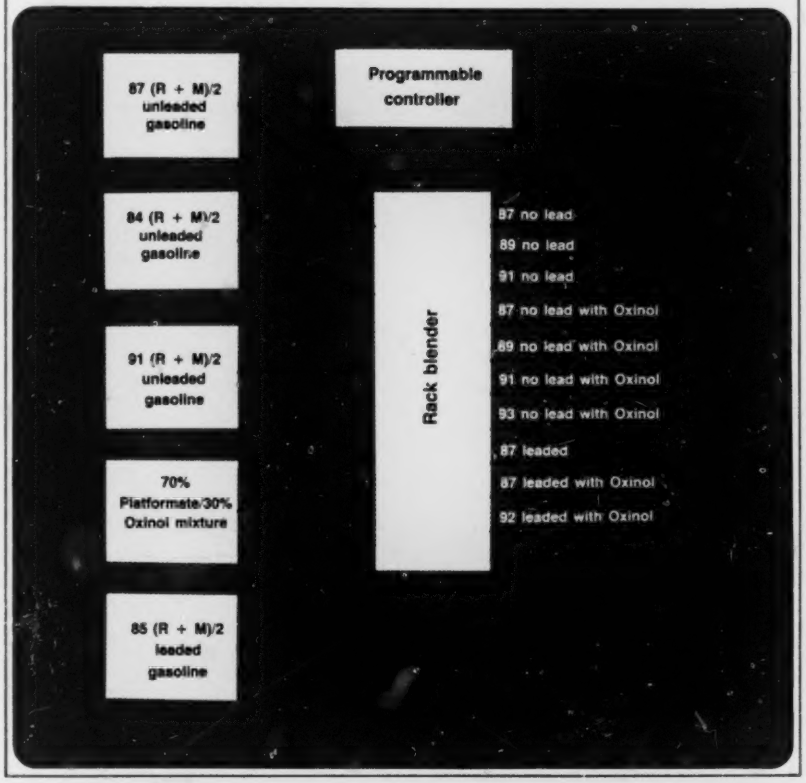
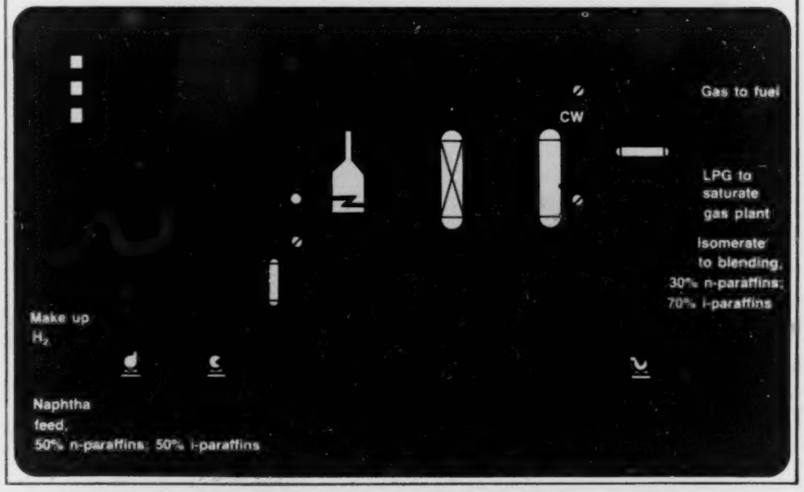

87 (R + M)/2 unleaded gasoline
Programmable controller
84 (R + M)/2 unleaded gasoline
91 (R + M)/2 unleaded gasoline
70% Platformate/30% Oxinol mixture
85 (R + M)/2 leaded gasoline
Rack blender
87 no lead
89 no lead
91 no lead
87 no lead with Oxinol
89 no lead with Oxinol
91 no lead with Oxinol
93 no lead with Oxinol
87 leaded
87 leaded with Oxinol
92 leaded with Oxinol

Fig. 2

Isomerization unit is revamped reformer


Gas to fuel
CW
LPG to saturate gas plant
Isomerate to blending, 30% n-paraffins; 70% i-paraffins
Make up H₂
Naphtha feed, 50% n-paraffins; 50% i-paraffins

maintain pool octane at the 0.5 g/gal TEL level. However, alternative octane sources in addition to CCR Platforming were required to maintain pool octane after Jan. 1, 1986.

**Lead banking.** Taking advantage of the opportunity under the EPA's TEL "banking" rules, by generation or purchase of TEL credits for use through 1987, not only allows time to establish other programs to maintain pool octane, but also offers a short-term economic octane alternative itself.

Any refiner short on pool octane can use credits either to avoid sale of low-octane components into what could be a distressed market, or to reduce dependence on expensive blend components. Refiners with sufficient pool octane can also benefit from the use of TEL credits to produce higher volumes of premium gasoline, upgrade low-octane stocks available at distressed prices, or simply take advantage of the higher incremental octane improvement available at lower TEL concentrations.

La Gloria acquired TEL credits by blending below maximum allowable TEL levels and by purchasing credits from other refiners and blenders. During 1985, the Tyler refinery was able to generate 9.8 million g of credits by using less than the maximum amount of TEL allowed.

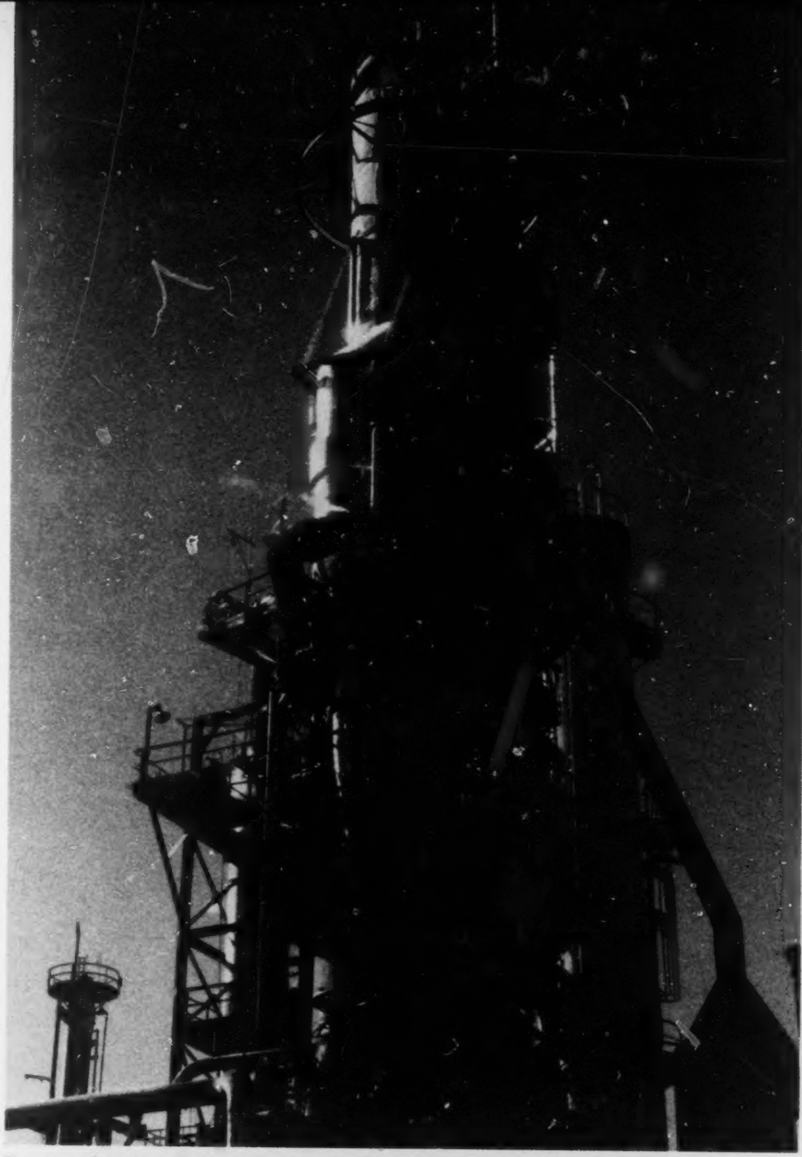
The opportunity cost associated with the generation of these credits was calculated monthly by a gasoline blending linear program capable of optimizing TEL level. This program, licensed by Wright, Killen & Feldman Inc., was extensively utilized to evaluate the potential value of the credits after phasedown as well.

All refinery-generated credits were inventoried at their opportunity cost. This cost is then allocated in future months as the credits are utilized. A small amount of credits was also generated at La Gloria midwest marketing terminals that blend ethanol and/or butane. About 867,000 g were inventoried at zero cost from these operations.

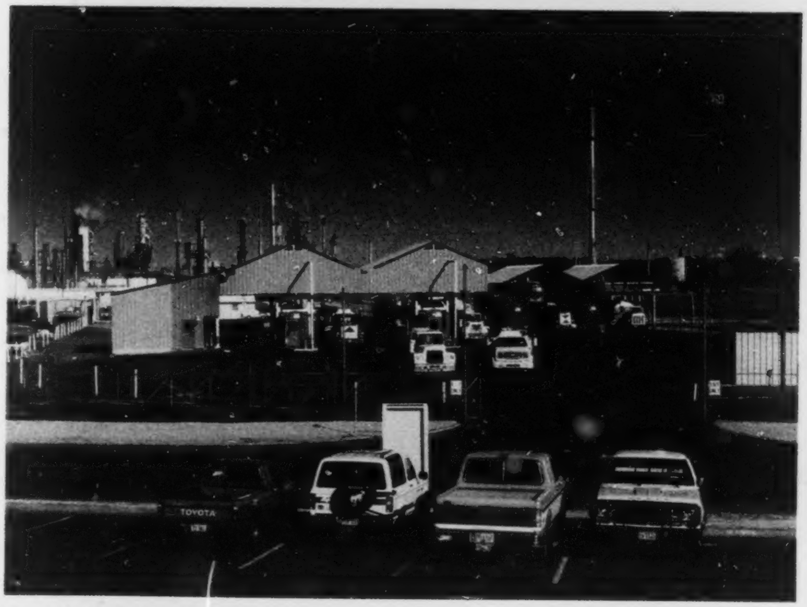
La Gloria also purchased 51.1 million g of TEL credits from other refiners and blenders. These credits were also inventoried at their purchase price, resulting in a total TEL bank of about 62.8 million g.

Since April 1985, La Gloria has banked sufficient TEL credits to meet its expected requirements through 1987. It is anticipated that these credts will return 150% of inventoried cost.

It was also determined that the credits would return revenues equal to cost under "worst-case" conditions. The true value of these credits is still highly dependent on the future gaso-



**Octane enhancing catalyst** was tested in this UOP stacked fluid catalytic cracking unit.



**View of La Gloria's loading rack** with the Oxinol rack shown at the extreme left.

line market.

La Gloria is presently utilizing about 2.5 million g of credits/month until other programs come on-line to ensure ample production of premium unleaded gasoline, and to avoid sales of low-octane streams at less than economic value because of low pool octane. It is estimated that these credits have been worth 154% of their inventoried cost.

After other octane-producing programs come on-line, remaining credits will still have the potential to produce revenues far in excess of their inventoried cost.

The continued economic production of leaded regular gasoline is a likely use of TEL credits. Leaded regular demand should remain constant if the price does not exceed that of unleaded regular by more than 1¢, due to the difference in octane.

It is also possible that there will be a small market niche composed of owners of older vehicles with a demand for leaded gasoline even at a premium price. An opportunity for higher margins will exist for refiners willing and able to continue to supply leaded regular to this niche.

The Tyler refinery was one of the last to discountinue leaded premium production in 1980, due to a very high regional demand that supported the high margins associated with small volumes.

The credits may also be used to divert higher-octane blend components to the production of additional unleaded premium gasoline or to blend lower priced natural gasoline and light naphtha into the gasoline pool.

The access to the petroleum products spot market provided by the Texas Eastern products pipeline, and the local availability of natural gasolines and condensates from the East Texas field, provide the Tyler refinery a great deal of flexibility in the use of its credits. Finally, with its other programs on-line, the company would be in a position to sell any remaining credits should demand make that alternative attractive.

**Octane catalysts.** New fluid catalytic cracking (FCC) catalysts formulated to increase the octane of FCC gasoline are being offered by all major catalyst suppliers in response to TEL phasedown, and have quickly generated great interest in the refining segment. La Gloria, along with a majority of refiners, has begun to utilize some form of octane catalyst in its UOP stack unit, with mixed results.

The 18,000-b/d unit was converted to riser cracking in the 1960s and typically operates at high conversion (75 to 85%) with a minimal clarified oil yield. Due to its carbon steel construction, the reactor temperature is limited to 980° F. The regenerator temperature is limited to 1,265° F. in the dense phase, and 1,300° F. in the dilute phase, for the same reason, requiring partial combustion operation.

To maintain stable operation in this mode, La Gloria has generally utilized a high-activity, bottoms-selective catalyst to process its FCC feed (which contains up to 20% coker gas oil) with good results. In an attempt to maintain a similar operation with improved FCC gasoline octane, an octane catalyst similar to our current catalyst was tested in the unit.

The benefits from operation with octane catalyst were quite dramatic. FCC gasoline octane increased from 87.5 RONC to 92 RONC as the octane catalyst concentration in the unit approached 100%.

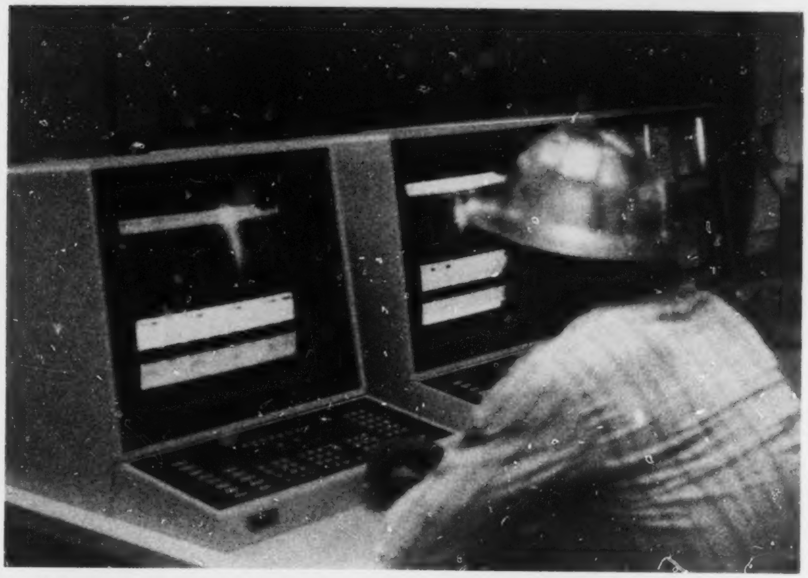
The olefin content of the $C_3/C_4$ yield increased from 50% to 70%. Although conversion dropped from 86% to 78.5%, most of the shift was to the distillate yield; clarified oil yield increased slightly.

As would be expected, alkylation capacity became tight even at moderate FCC charge rates. But the overall yield changes were satisfactory.

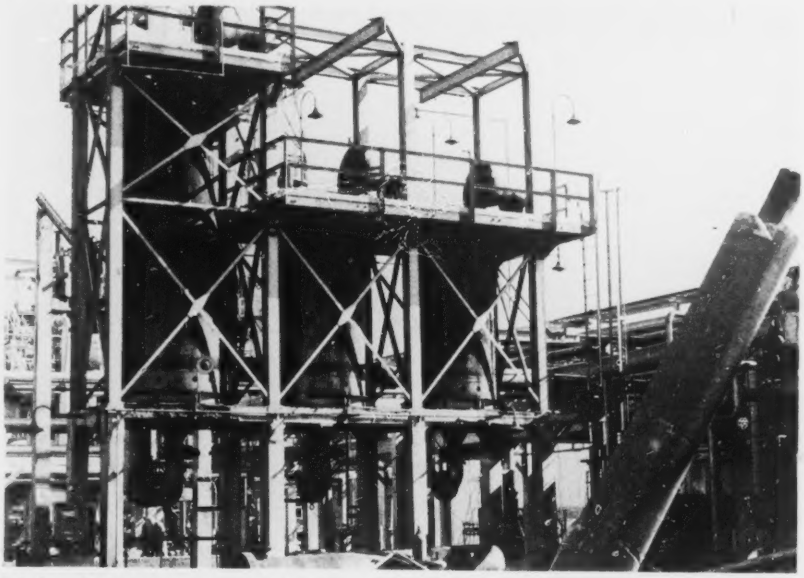
Unfortunately, with the expected yield and octane changes came a very unstable regenerator operation. As the new catalyst approached 100% of cir-

**Volume display and entry** keyboard is shown at left in this view of the rack blending system.

**Bank of meters** is used for blending Oxinol into finished gasoline blends.



**Control console** for Moore Mycro distributed control system that will be installed for the isomerization unit.



**Existing Platformer reactors** used for the installation of the once-through isomerization unit.

culating inventory, the dense-phase temperature fell from 1,265° F. to below 1,220° F., and the dilute phase temperature increased to 1,320° F. from 1,270° F.

The carbon level of the regenerated catalyst rose considerably—the unit frequently fell behind in burning, creating a significant number of upsets. Operation could not be stabilized, even with the addition of 15 lb of combustion promoter/ton of fresh catalyst.

Discussions with other refiners testing similar octane catalysts in UOP stack units indicate that the regenerator problem was not limited to our specific unit or catalyst selection. Similar problems were experienced by several refiners using octane catalysts from other vendors in UOP stack units. With this information, the Tyler refinery returned to the original, non-octane catalyst previously utilized.

When the concentration of octane catalyst was reduced to 50%, regenerator stability was again achieved, and FCC gasoline octane was reduced by only one number.

The unit is presently operating on a 50/50 mix of these two catalysts quite well. This catalyst blend will continue to be used until pilot plant studies indicate another octane catalyst or catalyst blend (using an octane catalyst or the Mobil ZSM-5 zeolite additive) is more suitable for our unit.

**Alcohol blends.** La Gloria has been exploring, with initial success, alcohol blendstocks. During the past 2 years, the company has been "topping-off" gasoline sold at its Midwest terminals with ethanol, essentially for tax benefits. Beginning this year, topping operations with natural gasoline and ethanol will allow capture of octane benefits as well at these Midwest terminals that deliver up to 150,000 bbl/month of blended gasoline.

Alcohol blends are also being tested in the company's major market, the Tyler/East Texas area. With La Gloria's refinery terminal supplying 72% of the gasoline consumed in this area through direct sales to independent wholesalers and exchanges with major oil companies, the company believed that significant volumes of alcohol-blended fuel could be successfully marketed.

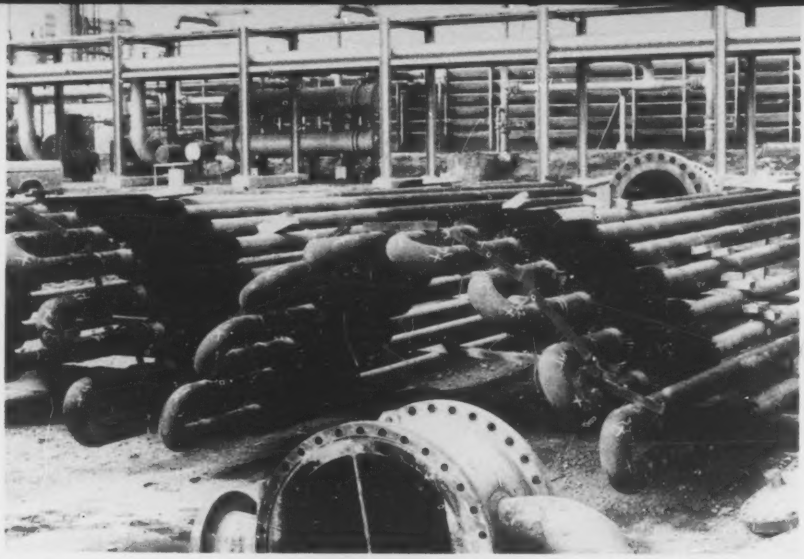
Customers were invited to a presentation on ethanol and Oxinol blendstocks, and were surveyed for initial acceptance.

It was found that independent wholesalers were quite interested in the blended fuel provided there was economic incentive. Jobbers marketing fuel under a major brand also expressed interest, but indicated any decision would be contingent on agreement by their major oil company supplier. Oxinol was found to be the choice of the customers, primarily due to the ARCO sales effort, which included preparation of the stations at no expense to the customer.

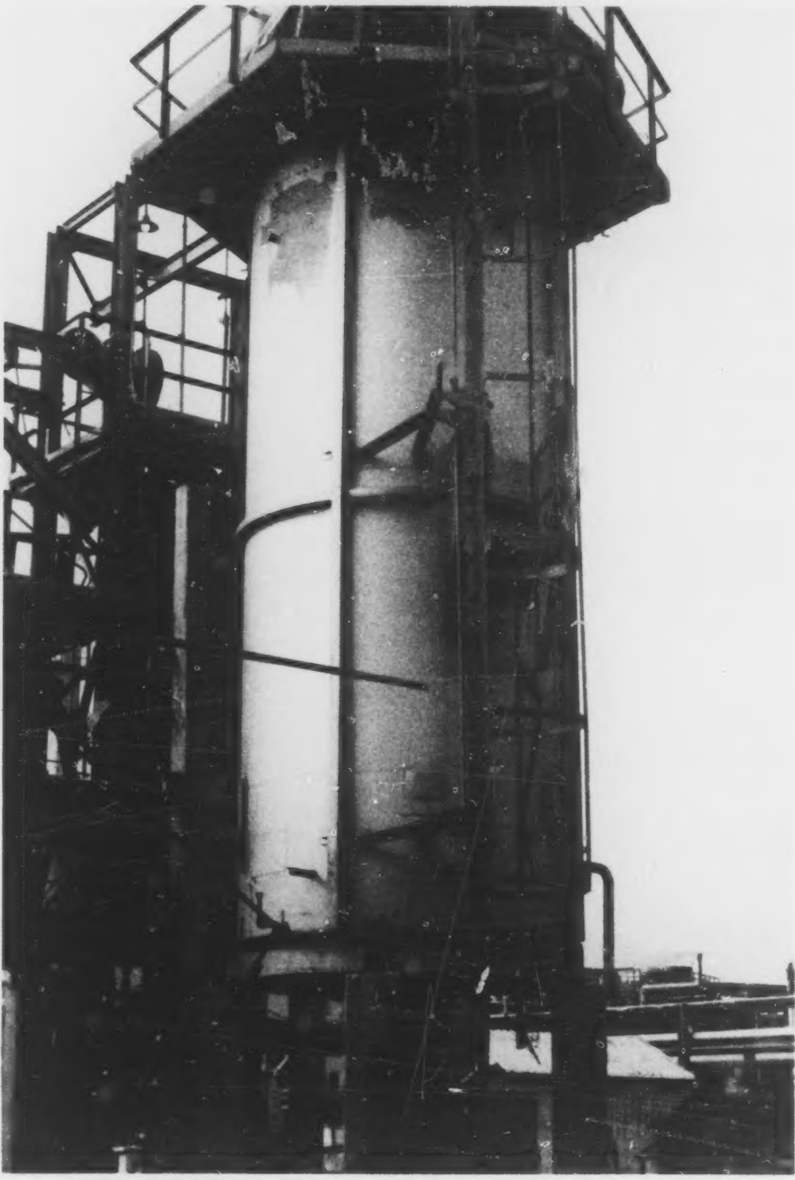
With an apparent market awaiting, the next task was to implement blending in the shortest time at the lowest possible cost. A taskforce composed of members from engineering, quality control, and marketing quickly determined that the most rapid and inexpensive approach was to blend the product at the rack, utilizing the present finished gasolines, Oxinol, and some type of subgrade gasoline.

The system finally installed included all three finished gasolines: a 70% high octane, a low Rvp Platformate/ 30% Oxinol mixture, and an 84 octane finished gasoline. These components can be blended into fuels meeting all La Gloria specifications. The system is capable of blending fuels with or without Oxinol, leaded or unleaded, at octane levels ranging from 84 to 93 research + motor/2 (R + M)/2 (Fig. 1).

Blending is accomplished by sequentially loading the various components according to pre-set blend recipes for each grade of gasoline offered. When the customer enters the desired volume and a three digit product code at the load spot, an Allen-Bradley programmable controller activates individual component meters.



**New heater coils** for the isomerization unit were fabricated from surplus heater tubes.



**Surplus 8 MMBTU/hr heater** used in place of existing reformer heater.

These deliver the proper volumes dictated by blend recipes stored in the controller's memory. The desired grade of fuel is blended directly into the truck.

Since October 1985, rack blending has been successfully utilized at the Tyler refinery terminal to deliver alcohol-gasoline blended fuel. The system was implemented in only 5 months at a cost of $150,000.

Several key considerations led to the choice of the rack blending approach and were responsible for its rapid and inexpensive installation.

Conversion of only one of the five gasoline load spots at the terminal was required.

Only one additional existing tank at the refinery was required for the Oxinol-Platformate mixture. The existing 89-octane unleaded gasoline sales tank could be used for the suboctane gasoline because this mid-octane product could now be blended by the new rack system.

The existing loading dock programmable controller was expanded to allow control for the blending function. Finally, only one alcohol-hydrocarbon mixture, isolated in a single tank, was required, minimizing exposure to phase separation.

Since deliveries began, Oxinol-blended gasoline sales have steadily increased to over 32,000 bbl/month through nearly 40 area stations without a single customer complaint. With the dramatic price drop in crude oil and refined products, economics of utilizing alcohols as gasoline blend components have been severely impacted. It is doubtful that La Gloria can continue to economically market these blended fuels at present gasoline prices.

Regardless of the current economic situation, the company has demonstrated that alcohol-blended fuels can be successfully marketed under the proper circumstances. The Tyler rack blender remains a very flexible tool in the test marketing of various octane grades of gasoline and the use of other blend components.

**Isomerization.** In the center of the TEL phasedown activities at the Tyler refinery is the revamping of an idle, fixed-bed catalytic reformer to a once-through light naphtha isomerization unit (Fig. 2). This revamp is especially important to La Gloria's phasedown efforts because it will allow upgrading of an important gasoline-bending component that presently has limited use in unleaded gasoline.

Previous attempts to utilize more than 5% light straight-run naphtha in unleaded blends have generated numerous customer complaints about gasoline quality. While unleaded gasoline with more than 5% meets or exceeds all of La Gloria specifications, a very poor "front-end" octane results, influencing customer perceptions about quality.

As little as 0.4 g/gal of TEL in leaded regular gasoline blends sufficiently improves light straight-run naphtha octane and the "front-end" octane of the blend to satisfy the majority of customers. This is evidenced by the lack of complaints directed at the leaded blends.

Once-through isomerization of light straight-run naphtha improves the octane of this material to the same degree, making this process option a viable method for increasing the amount of light naphtha that can be used in the unleaded pool, while maintaining gasoline quality. Should significant quantities of this blendstock exist, pool octane can be improved by over one full number.

Isomerization was the logical choice for the Tyler refinery for several reasons. Light naphtha composes a significant portion of the gasoline pool. With condensates and natural gasolines readily available from the local East Texas field, even greater volumes of light naphtha can be included in the pool, if isomerized.

An idle, fixed-bed catalytic reformer at the refinery, of sufficient throughput, ensured that light naphtha isomerization would be cost-effective.

With the solid concept of revamping an idle reformer to once-through isomerization, comes the decision of which catalyst to use. After thorough study of the available alternatives, the zeolite-type catalyst was chosen to be the best candidate for use. This rugged catalyst is much more tolerant of operational upsets and requires a lower investment because feed drying and off-gas treating are not needed.

A decision was then necessary on which zeolite-type catalyst: the commercially proven Shell Hysomer catalyst, or the new UOP I-7 catalyst.

After considerable study, the UOP I-7 catalyst was chosen because it was determined to be equal to the Hysomer catalyst in performance, it carried no royalty cost, and there appeared a minimal need for a UCC TIP unit in the near future.

UOP also offered an additional inducement, with an attractive service agreement credit. Once the catalyst was selected, the final design and equipment needs could be established.

The 5,000 b/d UOP Platformer, built in 1954, has been idle since the first quarter of 1983. The unit was virtually idled by the start-up of the new 12,000 b/d CCR Platformer in 1980.

## The author. . .

**Jones**

James W. Jones is manager, engineering and planning at La Gloria Oil & Gas Co.'s Tyler, Tex., refinery. He directs all engineering activities at the company.

Jones began his career in 1976 at the Tyler refinery as an assistant engineer performing numerous technical services, project engineering, and economic evaluations for all major process units. In 1984, he was promoted to manager, refinery planning, to establish and maintain a comprehensive refinery planning system for all aspects of the refinery.

Jones co-authored a paper presented at the NPRA Computer Conference, New Orleans, October 1985, and he was a panelist at the 1985 NPRA Q & A session on refining technology.

Jones has a BS in chemical engineering from the University of Texas and an MBA from the University of Texas at Tyler.

Though from a strict process flow standpoint little modification was necessary, a great deal of revamp was still required to upgrade the 30-year-old unit into an efficient and easily operable isomerization unit. Fortunately, most of the major equipment was either repairable or easily modified.

Additional idle equipment in suitable condition was also available which limited new equipment purchases to charge pumps, instruments, and a new 10 psig pressurized storage tank for isomerized product rundown.

The existing products separator and stabilizer system was suitable, although some tray repair was necessary. The three carbon steel reactors were in excellent condition and, with internal liners removed, provided the necessary volume required for a proper space velocity.

With the exception of the products condenser, all existing heat exchangers were usable after some minor retubing work. Replacement exchangers for product condensing, and additional exchangers required to improve the thermal efficiency of the unit, were all surplus items located at the refinery or other company facilities. The additional exchange surface was included for supplemental reactor feed-effluent and stabilizer feed-bottoms heat recovery.

The existing Clark three-cylinder reciprocating compressors previously used for hydrogen recycle were easily revamped to a combined make-up/recycle machine for the isomerization process. A single cylinder was converted to act as a hydrogen makeup compressor. The other two cylinders are used for hydrogen recycle.

A single stage make-up design was made possible by discharging directly to the products condenser—the location of lowest possible pressure. The make-up suction drum was a relocated surplus vessel requiring no modification.

The existing UOP three-compartment heater, common to units of this vintage, was much too large for the small amount of heat required for the isomerization process. This heater was also in quite poor condition.

An existing idle heater, available in the refinery, was determined to be the proper size for the new isomerization service. However, new tubes of different metallurgy (C, 1/2Mo), and significant rework were needed.

This revamp was found to cost as much as a new heater, but could be accomplished in a much shorter time. Considering the short project timetable of 6 months, the revamp approach was chosen, allowing greater control over the completion and delivery of this equipment.

New charge pumps were required because those used by the old Platformer were shared with another fixed-bed reformer still in operation. Although field instruments and control valves were still operable, new equipment was installed to improve process operations.

Connection to a distributed control system, being installed with another project, made it possible to upgrade the isomerization unit control at a very modest cost. La Gloria found through earlier experience that installation of effective distributed control requires good field instrumentation. Remaining expenditures were limited to piping revamps and the new 20,000-bbl rundown tank.

The attractiveness of once-through isomerization as an economic source of additional octane for La Gloria rests with its inexpensive operating and capital costs. Operating costs are expected to be less than 10¢/octane-bbl.

Assuming a suitable interest rate for the $2,600,000 capital invesment, the total cost of isomerization should not exceed 15¢/octane bbl.

With present price differentials at 3-4¢/gal for premium unleaded, and the product grade flexibility of La Gloria, the refinery experiences octane-bbl values between 30 and 40¢ that result in a 16-month payout on its invesment. If additional light naphtha is available at a distressed price, the payout time could be reduced by several months.

With the successful implementation of these programs, the Tyler refinery will have the octane capability to produce up to 22% of its total gasoline output as premium unleaded after complete phaseout of TEL. Because octane requirements may be even greater due to limited success of one or more of these programs, or even greater market demand for premium unleaded, further study of additional octane sources is an on-going project for the company.

For example, the use of ethanol as an alternative to Oxinol can be easily implemented with the present rack-blending system, while still maintaining the Oxinol blends. MTBE could also be blended into those grades not utilized by the rack-blending system.

Process additions that could result in increased octane for the gasoline pool are also viable sources, provided economics so dictate. As previously discussed, FCC octane catalysts can generate up to 50% more light olefin feedstock, potentially exceeding alkylation capacity.

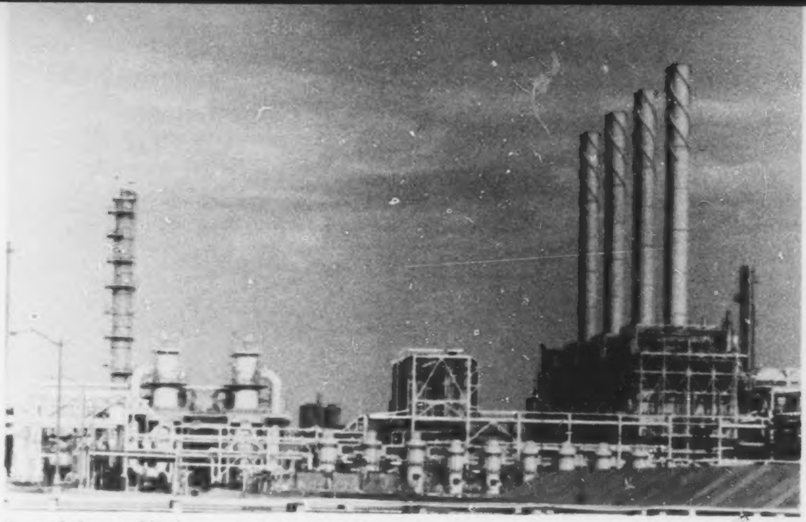
MTBE manufacture, or a dimerization process (such as IFP Dimersol or UOP Hexall), appears to be a rather low capital investment to handle the increased volume, and both generate products with higher gasoline blending values than their respective alkylate.

Recycle isomerization, via fractionation or molecular-sieve separation, presents a proven technological method for significantly increasing the octane by 7 to 10 octane numbers of a once-through isomerized light naphtha, and could raise the Tyler refinery's pool octane by a full number.

Through TEL banking, FCC octane catalysts, test marketing of Oxinol blended gasoline, and the revamp of an idle, fixed-bed catalytic reformer to a once-through isomerization unit, La Gloria Oil & Gas Co. is directly meeting the challenges of TEL phasedown. These projects not only fulfill minimum pool octane needs, but also provide the economic octane flexibility required by the competitive refining industry.

Through on-going studies of additional octane sources and improved planning, the company is preparing economic responses to continually changing product markets. La Gloria can, and will, remain economically competitive by maintaining its processing flexibility and market responsiveness, the essential characteristics of a successful small refiner. ▪

# Plant start-up programs in a developing nation



**One of the world's** largst single-train ethylene plants, Saudi Petrochemical Co.'s 656,000-ton/year unit at Al-Juabil, was brought on stream well ahead of schedule due in part to a well-conceived personnel development program (Fig. 1).

**M.H. Al-Morished**
**C.R. Carradine**
Saudi Petrochemical Co.
Al-Jubail
Saudi Arabia

The first plant in Saudi Arabia to make high-purity ethylene produced specification product on Oct. 7, 1984, ahead of schedule and below budget. It was the initial operating unit brought on stream in Saudi Petrochemical Co.'s multibillion-dollar petrochemical complex at Al-Jubail (Fig. 1).

The plant, designed to use ethane as a feedstock, has a nameplate capacity of 656,000 metric ton/yr, making it one of the world's largest single train ethylene plants. Start-up was achieved several months ahead of schedule without a lost time injury.

Final commissioning and start-up is a milestone event for any operation, but was especially significant with this plant in light of the unusual challenges faced. This success can be linked to the implementation of several key managerial programs and philosophies.

Saudi Petrochemical Co. is a joint venture between the Saudi Basic Industries Corp. (Sabic) and Pecten Arabian Ltd., a wholly owned subsidiary of Shell Oil Co. Sabic was created in 1976 to develop the primary and secondary industries to use Saudi Arabia's natural gas resources by producing a wide slate of commodity and speciality chemical products, fertilizers, and basic metal goods.

Initially, Sabic entered into partnerships with several established companies. The Sabic industries rely on the specialized manufacturing expertise of these partners, coupled with increasing numbers of university educated and vocationally trained individuals available in the country's workforce.

Saudi Petrochemical Co. is one of Sabic's 12 first-generation projects. It was formed to construct, start up, and operate the single large petrochemical complex on the east coast of Saudi Arabia.

The complex is part of Al-Jubail Industrial City, a totally new manufacturing center complete with transportation, residential, communication, and support facilities. Saudi Petrochemical's slate of chemical products includes ethanol, ethylene dichloride, caustic, chlorine, styrene, and ethylbenzene. Ethylene is required as a feedstock for most of these products.

From its point of inception, the tasks faced by the new company were formidable: coordinating the engineering and construction contractors, developing the necessary procedures, acquiring an effective workforce, and rapidly developing Saudi nationals at the managerial, professional, and wage levels. All this had to be accomplished within the framework of a young and developing company.

Design and construction were provided by two large U.S. engineering and construction firms. The major portion of the operating units were constructed in Japan, divided into modules and shipped to the Al-Jubail location to be assembled. Individual module units were large, approaching 2,000 metric tons in weight. Special considerations for module handling had been designed into the newly constructed port and roadways serving the Al-Jubail industrial area (Fig. 2). Construction began in September 1982.

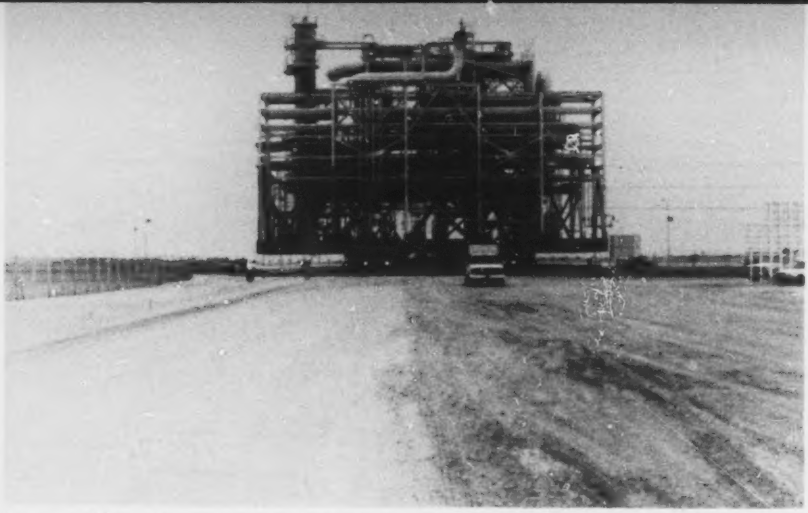
While construction proceeded, the operating organization began assembling a multinational start-up staff and molding it into a functioning team. While the experience of the ethylene section is related here, similar activities were taking place in the other product units.

**Organization buildup.** The ethylene start-up organization (Fig. 3) was built up over a 3-year period, beginning in 1981. The plan for the operating department comprised two sections in parallel development, reporting to a single department manager. The pyrolysis section had responsibility for the feed, furnace, compression, and acid gas treating equipment. The light olefins section comprised the drying, refrigeration, purification, and product storage operations.

Each section was headed by a manager and included an operating superintendent, a training coordinator, and a maintenance coordinator. Field activities were the responsibility of the superintendents. Reporting to them were the shift supervisors who in turn directed the work of the operating technicians.

The position of training coordinator was established to handle the significant training requirements, particularly those associated with the charge of rapidly developing Saudi nationals. These individuals were responsible for organizing effective training programs and coordinating the personnel and materials required to provide the training. They worked with technical, operations, safety, and other groups to meet the training requirements specific to the ethylene plant. General training in operations skills for the operator trainees was provided by the company training and development department.

The maintenance coordinators served as the interface between the operations department and the complex-wide maintenance support, warehousing, and procurement organizations. Some of the functions of this position are: providing detailed estimates of craft support required to meet start-up schedules, defining operating material requirements; reviewing spare part inventory plans, setting work priorities, and generally aiding



**Large module units** were constructed in Japan and shipped to the plant site for assembly. Special port and roadway provisions were included in construction of the Al-Jubail industrial area so that the modules could be transported successfully (Fig. 2).

in the effective use of maintenance manpower.

An additional position, start-up coordinator, existed in the department management structure. The start-up coordinator reported directly to the department manager and functioned as a liaison for bringing together interdepartmental activities and coordinating ethylene activities with other organizations of the complex. Examples of start-up coordinator activities are the integration of system-by-system commissioning activities into an overall efficient progression, and meshing the ethylene unit's steam, water, and other utility needs with the complex-wide system start-up schedule for these systems.

Two technical sections, one process engineering and the other support engineering, were devoted exclusively to ethylene. The role of the process engineer was concerned with onstream variables, process dynamics, processed material properties, and overall unit system function.

Support engineering dealt with the specific construction and function of each separate piece of equipment. For example, the inability of a fractionation column to reach capacity operation due to a heat input limitation would be a process engineering problem; the inability to reach capacity due to a poorly performing pump would be a support engineer's concern.

The support engineer was also the interface point for various technical specialties such as rotating machinery, inspection, and materials engineering. The process engineer provided the interface for the quality control and control systems functions.

Each engineering section had a manager that administratively reported to a plant-wide department manager for that function. These section managers, however, were functionally responsible to the operations department manager. It was planned that the technical and operating staffs be integrated to develop a close working relationship. The goal was to ensure quality in all activities by providing adequate technical and operations review and input from the point of initiation.

**Workforce make up.** The workforce plan set the number of people in the ethylene operating department and directly assigned technical staff at just above 130. The plan was developed not only to meet the need of putting the plant in service but also to provide for the rapid development of the Saudi employees.

Consequently, the staff included approximately 40 Saudi operator trainees. The trainees were assigned to experienced field employees to gain commissioning and start-up experience.

About 10% of the individuals would perform management or coordination functions, 15% would serve in technical positions, and another 15% be involved in field supervision. The rest, including all the operator trainees, would be assigned to direct field activities.

The technical staff planned for the ethylene unit consisted of process engineers and support engineers in approximately a 2:1 ratio. Peak levels of technical personnel would occur at the point of start-up to provide the planned round-the-clock coverage.

The factors of higher attrition and longer replacement timing typical for a Middle East location were taken into consideration in developing this workforce projection. Based on the experience of other companies operating in the Middle East, it was known that an expatriate workforce could have an annual attrition rate greater that 10%. Finally, because foreign relocation was involved, the lag time between interviewing potential replacements and the reporting date of a selected candidate could be 4 months or more.

The department manager, the operations section managers, the operations superintendents, and the process engineering manager were the first positions filled. Two supervisors with extensive ethylene background were soon added.

This group was located at the engineering contractor's office. Their function was to provide input of their commissioning and operating experience to the final phases of design, and to begin writing the commissioning and start-up procedures. These procedures were detailed and nearly complete by the end of the design phase.

Having a good knowledge of commissioning events at this point allowed much of the specific requirements to be designed into the plant at minimum cost. This up-front planning minimized field revisions such as valve and tie-in point additions during commissioning and thus saved both money and time.

In late 1982, the ethylene start-up organization relocated centrally in Houston with the company's other organizations. Overall planning and policy formation were begun for the engineering and operations division of the company. But the major task during this period was recruitment.

Most of the first line supervisory and the non-supervisory positions, both technical and operations, would be filled through direct hiring. Candidate selection was the responsibility of the department's managers and operating superintendents.

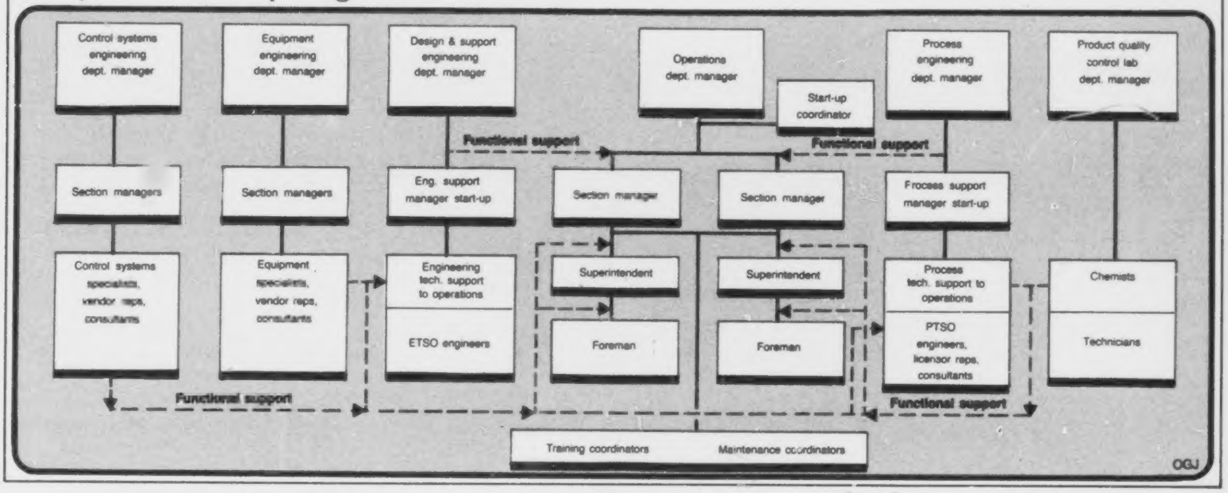
Eventually, almost two thirds of the department's positions were filled through recruitment from five different countries. The U.S., Canadian, U.K., and Indian job markets were targeted because of the availability of individuals experienced in the processing industries, particularly the ethylene process.

All operator trainees were Saudi nationals. The remaining positions were filled from within the partner companies or their affiliates.

Most of the newly hired technical and operations supervision staff joined the organization at the headquarters location. From mid-1982 until relocation to the plant site, ethylene technical and operations were involved in defining specifics such as commissioning activity bar charts: materials, utility, and support group needs; plant modifications and resolution of post-design follow-up questions; training requirements; feed/product specifications; and construction turnover crite-

Fig. 3

Ethylene start-up organization


Control systems engineering dept. manager
Equipment engineering dept. manager
Design & support engineering dept. manager
Operations dept. manager
Start-up coordinator
Process engineering dept. manager
Product quality control lab dept. manager
Functional support
Functional support
Section managers
Section managers
Eng. support manager start-up
Section manager
Section manager
Process support manager start-up
Control systems specialists, vendor reps, consultants
Equipment specialists, vendor reps, consultants
Engineering tech. support to operations
ETSO engineers
Superintendent
Foreman
Superintendent
Foreman
Process tech. support to operations
PTSO engineers, licensor reps, consultants
Chemists
Technicians
Functional support
Functional support
Training coordinators
Maintenance coordinators
OGJ

ria. In Saudi Arabia, preparations were being made by the construction contractor to receive the first plant module. A total of 34 modules, shipped over an 8-month period, were required to complete the ethylene plant.

Movement of ethylene personnel to the plant site began as plant construction reached the final phases. Recruitment and assimilation of the operating staff below the level of first line supervisor continued throughout this period.

The first field activity for the ethylene organization was inspection and acceptance of plant equipment from the construction contractor. This phase, commonly called "punch out and turnover," began in late September as individual plant systems reached construction completion.

In the initial commissioning planning, the concept of sequentially turning over critical systems ahead of the scheduled total plant mechanical completion date had been developed with the construction contractor. Early turnovers were especially necessary in the utilities systems in order to meet the critical-path requirements of other downstream systems.

The early turnover program, termed sequential completion, acceptance, and turnover (SCAT), divided the ethylene plant into 54 process-related systems. The cracking furnaces, the process gas driers and regeneration facilities, high pressure distribution steam distribution and the deethanizer fractionation column, and associated equipment are examples of SCAT systems. These component system divisions were not only used in inspection and acceptance, but continued through the commissioning phase to the point of start up.

Due to the success of the early turnover program, commissioning of many of the major SCAT systems were nearing completion by the time of total plant construction completion. Trash blowing and dry out of the cryogenic sections of the plant were completed within 3 months of total plant turnover and when initial equipment start-up activities such as cracking furnace initial heat-up and refrigeration system start-up had begun.

Specification product was produced 13 days after forward flow of cracked gas was established. This milestone was reached nearly 3 months ahead of schedule.

In the planning phase of the project, an expected ethylene production curve had been generated. It was based on the typical U.S. Gulf Coast experience, but was discounted for the location difference. As scheduled milestones began to be achieved early, a second curve was developed that represented the stretch goal. This production build-up closely paralleled Gulf Coast experience (Fig. 4).

Actual ethylene plant production not only exceeded the base plan, but also surpassed the stretch goal. The downstream plants were able to use this early production to facilitate accelerated start-up plans.

**Reasons for success.** The overall success of the commissioning and start-up effort was due to two factors: Effectively utilizing the significant experience and broad background diversity of the staff, and making allowances for operating differences in a developing area.

Primary examples are:

- Specific job roles were present in the organization that are not common in Western start-ups. Examples are maintenance/operations coordinator, start-up schedule coordinator, and training coordinator.

These postions were extremely valuable in setting early planning and maintaining the direction of the organization during commissioning and start-up. Through these roles, effective coordination and communication with support organizations were maintained.

- The ethylene organization was staffed earlier than usual. This afforded a greater operations input into the final stages of design. Additionally, the experienced operating superintendents and supervisors who would be carrying out the actual plant commissioning participated in the planning and procedures development for these activities.
- Experience and qualifications criteria during staffing were held stringent. Strict hiring criteria were set requiring experience in an ethylene-type facility for all levels.

Supervision levels required 5 years of specific ethylene experience, but many individuals had significantly more experience. Across the department, the average experience level was well over 5 years, representing over a dozen world-scale plants in several countries.

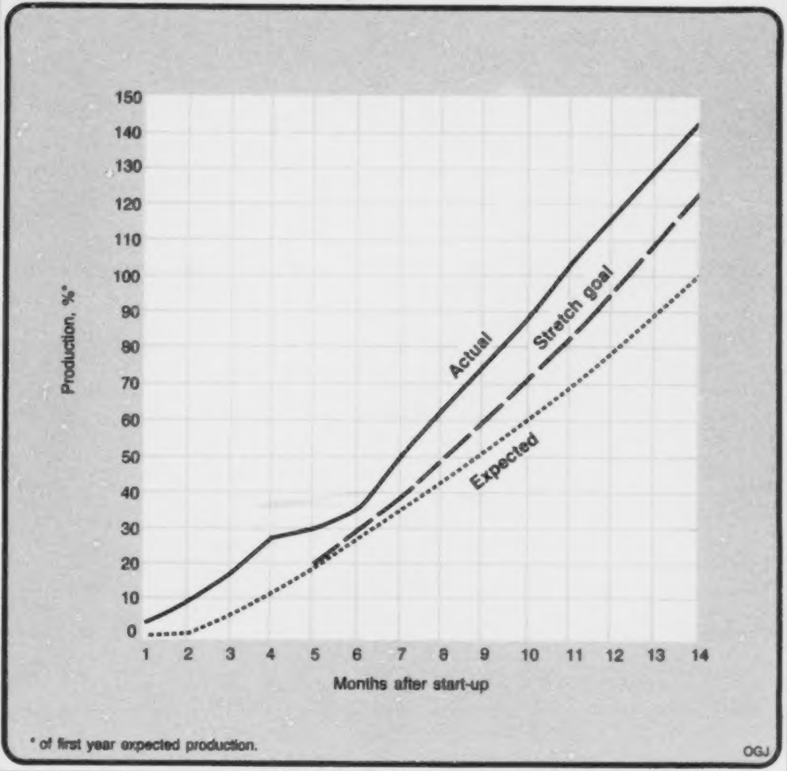
Proficiency in English was also a requirement for all expatriate workers. Saudi trainees received extensive language training before being assigned to the plant.

- Outside consultants and specialists were retained to conduct objective reviews. Experts in the areas of safety, operation, maintenance, and equipment performance provided an objective assessment prior to each major progress step in commissioning and start-up.

Examples of areas audited are: The

Fig. 4

## Ethylene production goals



* of first year expected production.

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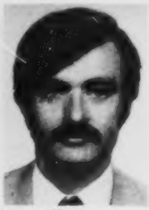
### The authors. . .

**Al-Morished**



**Carradine**

Mutlaq H. Al-Morished is operations manager of Saudi Petrochemical Co.'s chlorine and ethylene dichloride plants. He was a member of the process engineering group assigned to the ethylene plant start-up and later served as manager of ethylene process engineering. Al-Morished holds a BS degree in physics and mathematics from University of Denver and an MS of engineering from Princeton University.

Charles R. Carradine is planning manager at Saudi Petrochemical Co. He joined the company in 1983 as a member of the process engineering group assigned to the ethylene plant start-up. His previous experience was in various phases of olefins manufacturing with a major U.S. oil firm. Carradine holds a BS degree in chemical engineering from Louisiana State University and is a registered professional engineer.

effectiveness of the complex-wide maintenance system at the point of commissioning initiation, the completeness of start-up plans and procedures, and the overall readiness to start the ethylene plant that particularly emphasized the support organizations.

The outsider reviews were considered a major aid in attaining excellent performance in these areas.

- Team concepts were used during commissioning and start-up phases. This technique proved to be an effective way of utilizing the vast amount of experience available and still maintaining a unified organizational direction.

A commissioning team was set up and assigned to each SCAT system. Each team included a core group consisting of a representative from the operations, process engineering, and support engineering functions. Experts from the engineering specialties such as instrumentation and rotating equipment were brought into a team as needed. Having this diversity of disciplines assured that activities were reviewed from multiple perspectives.

The teams had the responsibility for putting together the plan for each assigned system. This task included performing a step-by-step field review of the prepared procedures and identifying the material and personnel resources required for implementation.

The team also prepared schedules and detailed maintenance items. Special procedures relating to chemical cleaning, catalyst loading, etc., were developed as necessary. Each team was responsible for providing management with an overall plan review and then scheduling the tracking. Once the tasks were fully defined, implementation became the primary responsibility of operations, with the team continuing to provide assistance and follow-up as the plan was executed.

The early commissioning of most systems can be directly credited to the efforts of these teams. Furthermore, through team formation during the early phase of commissioning, working relationships between operations and technical support were strengthened.

Benefits from team synergism continued throughout the start-up and initial operating phases; operations continued to seek out technical input and assistance in resolving problems and developing forward plans.

- Task forces were formed several times during commissioning and start-up to resolve critical areas of difficulty. The organization found the need to properly employ the expertise of various specialties, and yet in such a way as to not impede the progress of the numerous other activities occurring in parallel.

This concept worked well because management clearly placed the team in the lead role. Responsibility for resolving the issue of concern was clearly the team's, and team recommendations were almost always adopted and supported.

- The long lead time needed for material procurement was reflected in the warehouse stocking plans. Traditional assumptions of availability had to be reexamined. Many items that would be available from suppliers on an "off the shelf" basis in a North American or European industrial location required weeks or months to deliver to this remote plant site. Consequently, such items were warehoused. Although this resulted in a larger initial capital outlay for spare equipment and materials, benefits were realized in reduced expediting costs and production delays.

As start-ups of the highly sophisticated manufacturing processes in newly developed sites close to basic resource supplies become more frequent, techniques of managing these operations will be refined. The Saudi Petrochemical Co. experience has shown that with the adoption of certain fundamental organizational principles, high standards in commissioning and start-up can be achieved even in a remote location. ▪

# Tenneco upgrades natural gasoline

**Eugene K. O'Gorman**
Tenneco Oil Processing & Marketing
LaPorte, Tex.

Tenneco Oil Co. recently completed a natural gasoline upgrading project at its LaPorte, Tex., facility. The project was started in October 1985. The purpose was to fractionate natural gasoline and isomerize the n-pentane component.

Three factors made this a particularly attractive project for the LaPorte complex:

1. The phase down of lead in gasoline made further processing of natural gasoline desirable.
2. Idle equipment and trained personnel were available at the plant as a result of a switch of Tenneco's natural gas liquids (NGL) fractionation to its Mont Belvieu, Tex., facility.
3. The plant interconnects with Houston's local markets. It has pipelines to Mont Belvieu, Texas City, and plants along the Houston Ship Channel, as well as truck, tank car, and barge-loading facilities.

Here are the details on the operation of the facilities, the changes which were required to enable the plant to operate successfully, and how this conversion was completed in a timely fashion.

**Original facility.** Until October 1985, Tenneco fractionated NGL's that were fed directly from a pipeline. The process utilized a deethanizer, two depropanizers, two debutanizers, and two deisobutanizers. When economics were favorable, a Butamer unit was operated in conjunction with the fractionators (Fig. 1).

The plant history shows that the majority of the fractionating plant was built in 1956, 1957, and 1960. Energy conservation projects were completed in 1978 and 1979. The types of energy conservation used in the operations are an economizer on one debutanizer, and a heat pump on one deisobutanizer. The Butamer unit was installed in 1981, and the deethanizer was built in 1982.

Tenneco also operates an underground storage terminal at Mont Bel-

Fig. 1

Original fractionation and Butamer unit

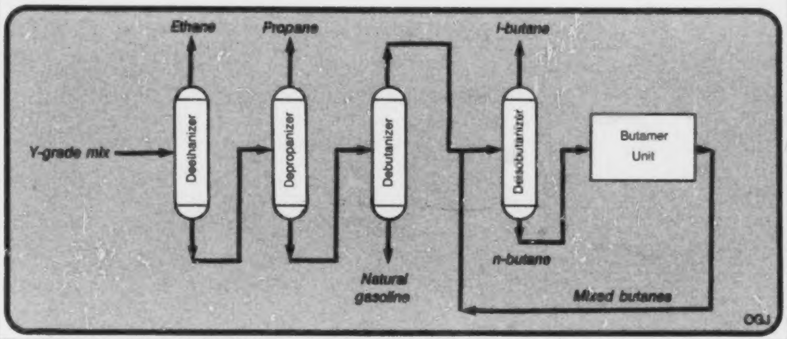

Ethane
Propane
i-butane
Y-grade mix
Deethanizer
Depropanizer
Debutanizer
Deisobutanizer
Butamer Unit
n-butane
Natural gasoline
Mixed butanes
OGJ

Fig. 2

New plant flow diagram

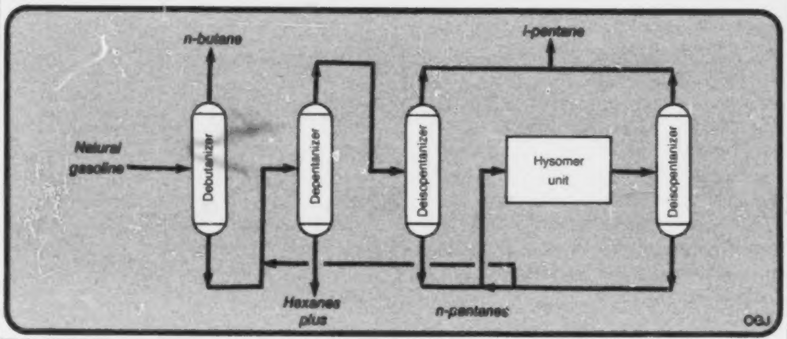

n-butane
i-pentane
Natural gasoline
Debutanizer
Depentanizer
Deisopentanizer
Hysomer unit
Deisopentanizer
Hexanes plus
n-pentanes
OGJ

Table 1

## Comparison of fractionator operating conditions

| | Service | Y-grade mix | Natural gasoline |
|---|---|---|---|
| **First tower** | | Deethanizer | Idle |
| | Pressure, psig | 300 | — |
| | Temperature top, °F. | 60 | — |
| | Temperature bottom, °F. | 275 | — |
| **Second tower** | | Depropanizer | Debutanizer |
| | Pressure, psig | 300 | 85 |
| | Temperature top, °F. | 143 | 144 |
| | Temperature bottom, °F. | 270 | 260 |
| **Third tower** | | Debutanizer | Depentanizer |
| | Pressure, psig | 150 | 50 |
| | Temperature top, °F. | 175 | 180 |
| | Temperature bottom, °F. | 298 | 275 |
| **Fourth tower** | | Isobutanizer | Deisopentanizer |
| | Pressure, psig | 85 | 26 |
| | Temperature top, °F. | 147-132 | 145 |
| | Temperature bottom, °F. | 176-148 | 158 |

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Based on a paper presented at the Gas Processors Association 65th annual convention, San Antonio, Mar. 10-12, 1986

Table 2

## Design and operating parameters of isomerization unit

| | |
|---|---|
| Feed gravity, °API | 0.6029 |
| Feed vapor pressure, Rvp, psia | 33 |
| Feed sulfur content, ppm total sulfur | 10-30 |
| Operating pressure, psig | 300-500 |
| Operating temperature, °F. | 500 |
| Feed weight hourly space velocity | 1-3 |
| $H_2$/HC ratio, mol/mol | 1-4 |
| $H_2$, scf/bbl | 70 |
| Heat of reaction | Slightly exothermic |
| Product gravity, °API | 0.6064 |
| Product vapor pressure, Rvp, psia | 43 |
| Catalyst regeneration | 2-3 Years |
| Conversion | 65-66% |
| Yield | 97-98% |

Fig. 3

Isomerization unit flow diagram

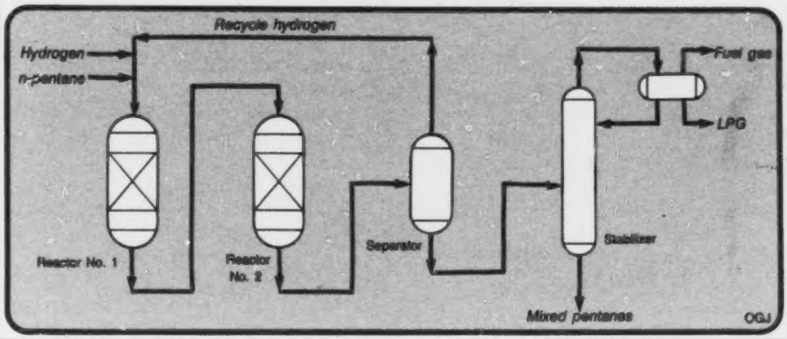

Table 3

## Feed and product qualities

| | Natural gasoline | Isopentane | Hexanes plus |
|---|---|---|---|
| Composition, liquid-vapor % | | | |
| n-$C_4$ | 2-5 | 3-5 | — |
| iso-$C_5$ | 25 | 93 | — |
| n-$C_5$ | 25 | 3-5 | 3-5 |
| $C_6$ | | — | 48-52 |
| $C_7$+ | 45-48 | — | 44-46 |
| Vapor pressure, Rvp | 12-13 | 20-21.5 | 4-6 |
| Octane: research | — | 91.8 | — |
| motor | — | 88.8 | — |
| (R+M)/2 | 68-72 | 90.3 | — |
| Distillation: IBP | 68 | 75 | 131 |
| 10 | 103 | 79 | 149 |
| 50 | 122 | 81 | 167 |
| 90 | 202 | 85 | 217 |
| EP | 262 | 94 | 297 |
| Paraffins | 84 | 99 | 67 |
| Olefins | 0 | — | 0 |
| Naphthenes | 12 | — | 26 |
| Aromatics | 4 | — | 7 |
| Naphtha value N+2A | 20 | 0 | 40 |

Table 4

## Plant flow rates

| | | Nominal design case | Fractionation limit case |
|---|---|---|---|
| Feed | Natural gasoline, b/d | 10,000 | 15,000 |
| Products | n-butane, b/d | 450 | 700 |
| | Isopentane, b/d | 4,950 | 7,450 |
| | Hexanes-plus, b/d | 4,523 | 6,750 |
| Byproducts | LPG, b/d | 45 | 73 |
| | Fuel, b/d | 30 | 45 |
| Hysomer | Feed, b/d | 3,925 | 5,900 |
| | Hydrogen, scf/bbl | 70 | 70 |
| Hysomer | Conversion | 65% | 65% |
| | Yield | 98% | 98% |

vieu, in addition to the pipelines and loading facilities previously mentioned.

**Fractionator operation.** Tenneco's natural gasoline upgrading project included fractionation of natural gasoline into four components: n-butane, n-pentane, isopentane, and hexanes plus. This project suited the existing fractionation towers. Table 1 summarizes a comparison of fractionator operating conditions, and Fig. 2 shows the new plant operating schematic.

The first tower is a debutanizer that was formerly a depropanizer. The tower operating conditions are similar.

For example, the operating temperatures are almost identical. The top and bottom temperatures are 143°-144° F. and 260°-270° F., respectively. The operating pressure of the debutanizer is 85 psig which is much lower than the normal operating pressure of a depropanizer. This pressure difference required changes to move the bottoms to the next tower. To accomplish this, larger piping and a larger control valve were installed.

The second tower is a converted debutanizer that now functions as a depentanizer. Operating conditions are similar and again, operating temperatures are almost identical.

The top and bottom temperatures are 175°-180° F. and 275°-298° F., respectively. The operating pressure of the depentanizer is 5[illegible] psig. Here, the difference in pressure did not cause any problems.

The third tower is a deisopentanizer which was a deisobutanizer. Again, operating conditions are similar. The operating pressure of the deisopentanizer is 26 psig. The operating temperatures are in the same range. The top is between 132° and 147° F., and the bottom range is 148°-176° F.

The lower tower pressure required a modification to move the n-pentane to storage or to the isomerization unit. To accomplish this, the bottoms of both deisopentanizers were connected to a spare accumulator. An existing pump was utilized to pump the n-pentane.

The n-pentane is not sold, but converted into isopentane in the isomerization unit. The n-pentane is circulated to extinction.

Instrumentation changes were minor. Orifice plates were changed where necessary. Calibrations were made during a turnaround, and final adjustments were made during start-up.

## The author. . .

**O'Gorman**

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**Isomerization.** Fig. 3 shows the basic flow scheme of an isomerization unit. The isomerization unit is now a Hysomer unit.[1] The plant originally operated as a Butamer unit and was designed to operate at a total feed rate of 8,000 b/d. Basically, the unit has fixed-bed reactors, a hydrogen separator, hydrogen compressors, and a product stabilizer. The reactor uses a vapor-phase system.

The noble-metal catalyst is sensitive to many of the impurities that normally poison catalysts, but has a certain tolerance for sulfur. Table 2 summarizes Union Carbide's (licensor of Hysomer unit) general operating conditions.

The feed composition is approximately 92% n-pentane, 5% isopentane, and 3% iso-hexanes. The feed contains sulfur in the range of 10-30 ppm total sulfur and no water.

In addition to the equipment shown, an existing hydrogen recovery unit (HRU) processes the unit's offgas. The HRU is not currently operating, but the final design conditions and minor modifications are under consideration, and it will be utilized. The only modifications associated with the isomerization unit were changing the catalyst and replacing the product piping to one deisopentanizer.

**Storage.** Significant piping changes were made in the storage areas. No new storage has been added, but at a later date, Tenneco plans to add more isopentane storage to optimize distribution of that product.

The conversion project was completed in a short time. The first phase of construction concentrated on piping modifications. Natural gasoline feed piping was laid to existing pumps. The gasoline storage was divided into natural gasoline (feed) and hexanes-plus (product) storage. The hexanes-plus product meter had to be replaced to handle a higher production rate.

The n-pentane product handling system was connected directly to the isomerization unit. Only minimal n-pentane storage was provided for upset conditions such as a power failure.

The most critical product-handling problem was isopentane. Consequently, all available pressure storage remaining was utilized for this service. A second phase of construction is planned for mid-1986 to increase the storage capacity for isopentane.

To accommodate the new product in existing tankage, it was necessary to rearrange tank usage. Propane storage was eliminated. Normal butane is now stored in the former propane storage tanks and isopentane is stored in the former n-butane storage tanks.

**Products.** In the natural gasoline upgrading operation, isopentane and hexanes plus are the two major products. The quality of the products and the specifications of the natural gasoline feed are shown in Table 3.

The objective of the natural gasoline project is octane enhancement. Generally, natural gasoline with an octane of 68-72 will not be used in gasoline blending in the low-lead environment. As a result of processing, the modified plant is producing isopentane (a gasoline blending component), with a 90.5 octane number.

The hexanes plus may be used as either reformer feed or petrochemical feedstock. Tenneco has thus far pursued the reformer feed market.

As an integrated oil company with a refinery on the Gulf Coast, Tenneco was able to begin operation without delay by using this outlet. Hexanes plus as a reformer feed is particularly attractive to a reformer producing aromatics such as benzene, toluene, and xylenes.

To meet the needs of the refinery, an in-line blending system was installed to mix isopentane and hexanes plus for barge delivery. The LaPorte facility continues to deliver purity products across its barge dock, truck, and tank car facilities, and by pipeline.

**Plant flows.** The plant flows are described in Table 4, which summarizes the basic design cases. Tenneco engineering established 10,000 b/d of natural gasoline feed and 4,000 b/d of Hysomer feed as the design case, with Hysomer feed as the limiting flow rate.

Since the fractionator feed rate may be as high as 15,000 b/d, the final production rate may exceed these volumes. Actual operation will determine maximum throughput capacities.

**Objectives.** This project met the objectives set for it:

- To effect a change from NGL fractionating to natural gasoline upgrading.
- To begin the operation of the natural gasoline upgrading facility in the fourth quarter 1985, recognizing a lead phase-down implementation date of Jan. 1, 1986. (Feed started to the unit Oct. 24, 1985, and products were being produced on specification by Oct. 28, 1985.)
- To use existing equipment, thus minimizing capital in the conversion. Total elapsed time from the beginning of the project to the start of operation was 6 months.

**Turnaround.** During a 17-day turnaround, the following steps were taken to make final modifications:

- One-half of the operators were converted to maintenance work. They were assigned specific work, such as repairing valves, cleaning and inspecting equipment, and changing catalyst.
- The catalyst was changed in the isomerization unit.
- Oil was changed in the heating-oil system to obtain a higher operating temperature.
- Personnel were trained to operate the new isomerization unit.
- Personnel were trained in the piping changes which were added to maintain operational flexibility.

All of the goals set for the facility have been achieved. The plant entered 1986 functioning as a natural gasoline upgrading facility, well able to compete in this new business venture.

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# OGJ REPORT

# Refining Technology

## Substitute materials to replace asbestos in refinery-service gaskets and packings

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Refiners have been able to successfully replace asbestos in many packing and gasket applications. The changeover has been driven by health concerns, refusal of product liability insurance to suppliers, and supplier concern over long-term availability of asbestos.

A great deal of purchasing and engineering effort is currently being expended to qualify and convert nonasbestos materials for gaskets and packings. The task has been complicated by a lack of objective performance criteria in existing industry standards.

The majority of industry standards has specified the use of asbestos-based products because operating experience has shown they work. The specification criteria which do exist typically are valid for comparing competitive asbestos products only, and do not correlate well when applied to unrelated materials.

The task of reliably and safely operating a refinery without asbestos-based gasketing and packing is progressing on three fronts:

1. Replacement with products based on materials such as flexible graphite and poly tetra fluoro ethylene (PTFE). Performance characteristics are well known, and sufficient historical operating data exist.

The initial cost of these materials is typically higher than asbestos-based products.

2. Trials and replacement with "new" materials such as Aramid or glass-fiber-based sheet materials and braided packing, or mica/graphite-filled, spiral-wound gaskets. The performance characteristics of these materials are not well known in comparison to asbestos.

As might be expected, users have experienced both success and failure. Supplier development efforts have concentrated on improving performance while keeping replacement costs competitive with asbestos products.

Table 1

## Physical properties of an endless, flexible-graphite ring

| Property | Approximate value |
|---|---|
| Bulk density, lb/cu ft | 100 |
| Ash content, % | 5 max |
| Melting pt., °F. | Sublimates @ 6,000 |
| Coefficient of friction with 8 psi loading against stainless steel | 0.05 |
| Permeability across thickness at 1 atm. and 70° F., darcys | 4 to $9 \times 10^6$ |
| Compressive strength, psi | 24,000 |
| Electrical resistivity @ 70° F.; ohm-in. | |
| Along length and width | 3 to $4 \times 10^4$ |
| Thermal conductivity, BTU-ft/hr-sq ft-°F. | |
| At 70° F. | |
| Along length and width | 80 |
| Through thickness | 3 |
| At 2,000° F. | |
| Along length and width | 25 |
| Through thickness | 2 |
| Thermal expansion (CTE), $10^6$ in./in./°F. | |
| 70-2,000° F. | |
| Through length and width | −0.2 |
| Through thickness | 15 |
| 2,000-4,000° F. | |
| Along length and width | 0.5 |
| Through thickness | — |

3. Development of performance-based standards and selection criteria which seek to permit meaningful comparison of competitive materials independent of their formulation.

The following materials are being used as replacements for compressed asbestos sheet, asbestos filler in spiral wound gaskets, and asbestos millboard in jacketed gaskets:

- PTFE
- Flexible graphite
- Aramid fiber with suitable binders and fillers
- Glass fiber with suitable binders and fillers
- Ceramic fiber with suitable binders and fillers
- Mica and graphite with suitable binders and fillers.

**Compressed sheets.** The direct replacement of compressed asbestos sheet products has been chiefly Aramid or glass fiber with inorganic fillers and traditional elastomeric binders. In general, these products have not matched the elevated temperature/pressure performance of "premium" compressed asbestos sheets.

They have been able to match the performance of the service-grade sheets manufactured from inexpensive short asbestos fiber. Several users have reported satisfactory results sealing utilities in ANSI Class 150 applications to 400° F. using materials from at least three manufacturers.

These materials require increased percentage of binder and inorganic fillers such as clay to achieve ambient temperature sealability, improved production on calendars, and/or limit the usage of higher cost fibers. A typical compressed asbestos sheet has 80% asbestos fiber, 10-15% elastomeric binder, and the balance inorganic fillers.

Aramid-fiber-based sheet has 5-15% Aramid fiber, 20-25% elastomeric binder, and the balance clay or other inorganic fillers. Glass-fiber-based sheets have similar percentages of elastomeric binder and inorganic fillers.

The decreased percentage of heat-resistant fiber has made them far more dependent on the integrity of the composite matrix, particularly the elastomeric binder. Test work reported by Ernst Sauter[1] documents the increased thermal degradation experienced by these materials.

The suitability of these elastomeric-dependent materials above 400° F. will be limited to conservatively designed and well-bolted joints, decreased pressure-retaining capability, and high kinematic-viscosity fluids. Intensive development by compressed sheet manufacturers has dramatically improved their capability to consistently produce these materials and has improved the material's temperature resistance.

While successful applications at temperatures up to 750° F. and 400 psi internal pressure have been reported, nonasbestos compressed sheets are not yet capable of being used in services over 400° F. without regard to application. Standardized test methods and more field experience are required to develop comprehensive application tables for these materials above 400° F.

Several users surveyed[2] reported switching to other gasket types to replace compressed asbestos sheet in applications where the present compressed nonasbestos sheets have been unsatisfactory due to chemical and or thermal degradation of the elastomeric binder. These include:

- Filled PTFE sheet
- PTFE envelope gaskets
- Expanded PTFE
- Metal or wire-inserted flexible graphite spiral-wound gaskets

PTFE-based materials provide superb chemical resistance up to 500° F., low permeability, and are available in several forms which broaden PTFE's application range. Expanded PTFE, available in tape form, enables sealing lightly bolted flexible flanges.

PTFE envelope gaskets utilizing a conformable core are well suited to rigid or irregular flanges which are relatively lightly bolted, e.g., glass or glass-lined systems. Filled PTFE sheet overcomes the cold flow problems associated with PTFE when exposed to the higher clamping loads required for the upper limits of Class 150 and Class 300 operating pressures.

Flexible graphite is very attractive as a gasket material due to its low permeability, conformability, and thermal stability. These characteristics provide a material which can provide a reliable seal over a wide range of flange pressures.

A properly confined flexible graphite gasket has the additional benefit of being inherently fire safe. It also has superb chemical resistance with the exception of strong mineral acids up to 980° F.

Above this temperature, exposure to oxidizing atmospheres, including air, degrades the material. It can be effectively shielded from the oxidizing media with metal inserts or by permeation of the sealed media protecting the graphite from air at high temperature.

Good operating data exist for the use of flexible graphite in both steam and hydrogen-rich hydrocarbon service at temperatures to 1,200° F. in spite of exposure to air at that temperature at the outer periphery of the pressure boundry.

Failures have resulted at these temperatures when exposed to oxidizing services, such as flue gas which has nearly 20% oxygen, and in neutral or reducing atmospheres where the sealed media has a higher molecular weight than air. In that situtation, the graphite is consumed from the outer pressure boundry where it is in contact with air towards the sealed media.

Flexible graphite as a compressed sheet replacement requires reinforcement so that it can be effectively cut and handled prior to installation. It can be adhesive bonded to wire

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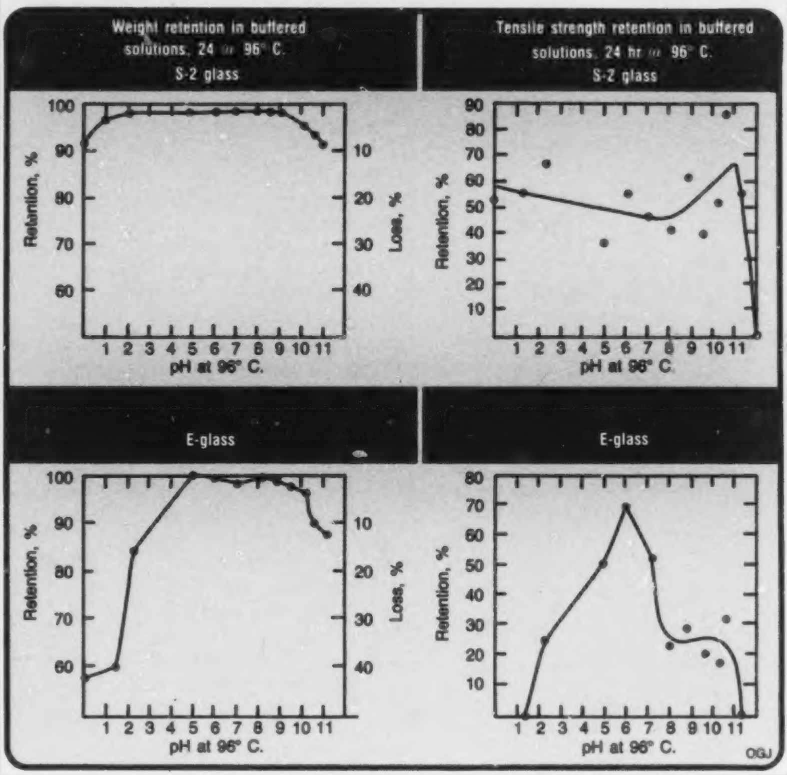
Based on a paper presented at the American Petroleum Institute 51st Midyear Refining Meeting, San Diego, Calif., May 12-15.

Fig. 1

## Caustic resistance of glass fibers



screen or metal foil, or mechanically bonded to a tanged metal core common to automotive gasket applications.

While thicker cores increase the handling strength of a graphite gasket, and provide the opportunity to profile the core to achieve blowout resistance, a thin core permits the use of economical steel rule dies for cutting, just as compressed asbestos sheet is now cut.

General refining practice over the past 10 years has been to increasing use of spiral-wound gaskets in place of premium compressed-asbestos sheet for services classed as lethal, highly flammable, or toxic. This has also applied to steam service above 400° F. The shift to nonasbestos materials has accelerated that trend.

**Spiral-wound gasket.** The replacement of asbestos filler in spiral-wound gaskets has been shared by increased use of PTFE, flexible graphite, and ceramic fillers, as well as development of new materials based on mica and mica/graphite.

Spiral-wound gaskets with PTFE or flexible graphite fillers capitalize on the desirable characteristics of both the filler materials and the gasket form itself.

The penalty for these benefits is that the initial cost of these gaskets is significantly higher than an asbestos filler. Mica or mica/graphite-based filler materials in spiral-wound gaskets are presently competitive in price to asbestos-filled spirals, and, properly formulated, are capable of higher performance levels than the asbestos fillers they replace.

PTFE-filled spirals are selected based on the chemical resistance of the filler material. While its low permeability gives good sealing results, the incompressibility of PTFE requires higher bolt loads (higher y or seating stress), better control of surface finish, and confinement to prevent gasket buckling on larger diameters (above 8-in. pipe), and higher pressure classes (above Class 300).

PTFE-filled gaskets have been used extensively by a number of valve manufacturers to ensure reliable performance in a wide range of chemical services with a single product. While not inherently fire safe, at least one manufacturer has produced a line of fire-safe ball valves utilizing PTFE-filled, spiral-wound gaskets.

Piping-flange gaskets for refining use are typically confined to hydrofluoric acid service where Monel, as a winding metal, is used in combination with PTFE. Chemical plant applications are more numerous where it offers the possibility of substitution over a broad range of applications up to 550° F.

Graphite-filled, spiral-wound gaskets offer significant performance improvements over asbestos-filled gaskets. Seating stress (y), and the load required to maintain a seal (m), are reduced.[3] They are more tolerant of flange surface finish variation.[4]

Graphite-filled spirals provide leak rates an order of magnitude or more below asbestos-filled spirals.[3] Substitution for existing chrysotile asbestos applications can be made without regard to application with the exception of service in strong mineral acids or above 980° F. in oxidizing service such as flue gas.

These advantages make flexible graphite appealing to standards-writing bodies, such as API and equipment manufacturers, where broad application and a high margin of reliability are paramount. The higher initial cost of flexible graphite-filled spirals has meant purchasing and operating personnel have been less willing to switch except in traditional problem applications.

Ceramic-filled spirals have been used with limited success for over 15 years. The fiber's chemical and high-temperature resistance make it a natural for consideration as an asbestos replacement.

Its high-temperature resistance to mineral acids make it the only viable product to replace Crocidolite (Blue African) asbestos for nitric acid service above 500° F. Unfortunately, the industry has been unable to produce a cost-effective, ceramic-based material which has the low permeability required for an effective spiral-wound gasket filler. Ceramic-filled, spiral-wound gaskets currently require conservative flange designs, excellent bolt up practice, and a tolerance for weepage.

Mica and mica/graphite-based filler materials have been developed since 1977. Micaceous minerals are attractive for use as replacement for asbestos because they are chemically similar to asbestos, hence similar chemical resistance is expected.

With small additions of web-forming fibers, it is possible to manufacture continuous sheets on conventional paper-making equipment. The key to successful spiral-wound-gasket performance is to produce a low-permeability paper for sealability and to keep the organic content low, preferably below 15%.

This enables maintenance of a reliable seal in the 500-1,000° F. temperature range common to spiral-wound applications. Achieving this target, with a material which has sufficient mechanical strength to facilitate gasket manufacture, has required significant development effort.

Just as with compressed nonasbestos sheets, there are currently differences in the performance of the various manufacturers' products, particularly in regard to elevated-temperature performance. Properly formulated, these materials have demonstrated equivalent or superior performance to asbestos in several years of refinery operating experience.

One refinery has reported applications in 1,400° F. flue gas and 1,100° F. hydrogen-rich hydrocarbon with superior results when compared to previous gasketing during 18 months of service.[2]

Steam service both in refinery and power generating utilities, to 1,100° F. in excess of 5 years for at least one manufacturer's product, has been reported.

Standardized test methods and more field experience are required to develop comprehensive application tables for these materials. However, the first few years of field experience are very encouraging.

**Valve packing.** The criteria for valve packing for use in refineries or petrochemical plants were determined many years ago. The standards used were for a packing that would withstand temperatures to 1,200° F., and pressures to 2,500 psi. At the same time it should be able to resist attack from a variety of fluids.

A reliable, economical packing that would be used by the valve manufacturer and yet be available to the refinery and easy to use and install by maintenance personnel on the job site is required. This packing was made of a AAA wire-inserted asbestos yarn with or without a plastic core, and it could handle the requirements, meet the standards, and more. That packing is no longer available.

Other materials must be found to meet the criteria. Each packing manufacturer puts his own idiosyncracy into the design, but each is working toward the predetermined goal. Most of the materials used as asbestos substitutes have not been on the market sufficiently long enough to be tested in every area of temperature, pressure, and fluid, nor have tests been completed, as against specification API 607, although this will be a reality within a short time. One approach for selecting which of the new nonasbestos products will be best adapted for the majority of applications is to examine the properties and then, based on this knowledge, make a choice.

## The authors...

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George R. McKillop is product manager of the packing division at John Crane–Houdaille Inc., Morton Grove, Ill. He is responsible for new product development working with the marketing department and customers. He has been with the company for 35 years working in the manufacturing engineering department and as sales manager of the packing division. McKillop earned a BBA in business administration from Northwestern University, and he is a member of the National Fluid Power Association.

There are many nonasbestos packings available in the lower-temperature range—up to 550° F., but more important is what is available for high temperature, high pressure? The base materials are as follows:

- Flexible graphite
- Carbon/graphite
- Glass fibers
- Ceramic fibers
- Polybenzamidazole (PBI)
- Metallics

There will be variations of these base materials as packing manufacturers, many times, will combine one or more materials to develop a packing that may have better chemical resistance, lubrication, or increase the tensile strength.

The first material, a flexible graphite, is made from expanded graphite to withstand high temperatures and high pressures. This material has a melting point that sublimes at 6,000° F.

Flexible graphite can be furnished either as a thin ribbon so maintenance can form the rings in a valve on the job site and/or the ribbon can be made into preformed rings to fit the valves. Flexible graphite rings can also be made of laminated sheet.

This was the first type of ring furnished from flexible graphite, and while they could be made very dense for good sealing, they required an interference fit because there was very little radial compression.

The rings of flexible graphite presently available can be furnished either as a high-density, 90 lb/cu ft density, or lower, 80 lb/cu ft density, depending on the equipment into which the material will be installed.

On new equipment or existing equipment in good shape, the higher-density material should be utilized because this type of ring emulates the older asbestos ring as far as compression is concerned, and there is sufficient radial compression to seal against the bore of the box and stem.

Additional advantages are that the higher-density ring has less tendency to adhere to the stem which means lower breakout friction as well as running friction. Further, with higher-density rings, there are less interstices left for moisture to adhere to, therefore, reducing the possibility of stem corrosion.

The lower-density ring, which can range from 70 to 85 lb/cu ft density, offers a ring that can be used in old equipment or reworked valves where the stem and bore no longer are the original dimensions. If the stem was 1 in., and the bore was 1½ in., a high-density ring made to the stem and bore diameter could be used. If the valve has been reworked and the stem is now 0.980 in. and the bore may be 1.562 in., a standard high-density ring will no longer give an effective seal.

This is where the lower-density, flexible-graphite ring, can and is used to affect a seal. The one drawback with the lower-density, is the ring compresses about 50 to 60% of its original height, thereby requiring twice the amount of rings to fill the stuffing box.

Because of its ability to handle high temperatures and wide variation in pH, low-density rings are being used in many severe chemical applications. One drawback with the flexible-graphite type of ring, is that it does not have a high degree of tensile strength and, therefore, it may have to be supported by the use of end rings or nonextrusion rings made of another material such as carbon/graphite ring and/or wire inserted glass or PBI. Table 1 shows some of the physical properties of an endless flexible-graphite ring.

A second, high-temperature packing available is carbon/graphite yarn; however, there are a number of different types on the market offering different performance levels.

Unfortunately, in a finished product, they look very similar. Pre-ox, a polyacrylic nitrile-base material can be used, but where oxygen is present it will lose 25% of its volume at 750° F. It would not be suitable for extreme high temperatures, pressures, or various fluids.

Carbon yarn or graphite, which is best for higher-temperature and higher-pressure applications, is carbon of at least 95% amorphous graphite, or graphite which is 99% carbon. These products use rayon as the base precursor in staple or filament forms, and can be used in conjunction with the flexible graphite or by itself.

Higher operating pressures, typical of Class 900 and above, require an inconel wire insertion in the carbon graphite packing.

This material is chemically resistant in a pH range of 0-14, so that it can handle most applications in a refinery without difficulty. In nonoxidizing applications, this type of yarn can withstand temperatures to 3,000° F. Another advantage is its low coefficient of friction, permitting low breakaway and running torques.

Most of the carbon graphite material being used in refineries today, for higher-temperature, higher-pressure applications, utilizes an inconel wire-inserted carbon/graphite jacket with a core consisting of graphite zinc inhibitor, carbon yarns, or other fibers.

A third material, glass fibers, is used in two forms: "E" glass and "S" glass.

"E" glass is one of the more common glass fibers and can be maufactured into a packing with or without an inconel wire insertion. It can also be used as a jacket around a plastic core of fiber glass, carbon, Kevlar, and other ingredients. The fiber glass itself is coated with a binder such as a Buna "S," neoprene, TFE, and graphite.

The drawback of "E" glass is its lack of resistance to caustics and therefore it is subject to attack during caustic cleaning of piping and valves. Also, at temperatures above 1,000° F., "E" glass loses approximately 50% of its tensile strength, negating its ability to handle high pressures.

"S" glass, developed by NASA, is the superior glass fiber in use today. It is caustic resistant, can handle temperatures to 1,500° F., and, with the addition of inconel-wire insertion, has a very high tensile strength.

This product is used as a jacket around a core material of graphite, fibers, and inhibitor. It is cost competitive with asbestos packing, and promises to meet the total requirements of an asbestos replacement.

Fig. 1 shows the difference of weight retention and strength retention between "S" glass and "E" glass, even in buffered solutions.

Ceramic fibers have been around for many years but unfortunately are not adaptable to the production of packings. Braiding this material is difficult, and the resulting product is brittle with little tensile strength. While the temperature resistance is good, the ability to withstand internal pressure is poor. Ceramic-fiber packing is not presently cost competitive.

A fifth material, polybenzamidazole (PBI), is a high-temperature fiber used in combination with other materials, primarily with an inconel-wire insertion as a jacket over a plastic core of material consisting of graphite, inhibitors, and various fibers. This packing is designed to handle high temperatures and high pressures, and is an accepted material for the valve manufacturer, as well as the maintenance man, because the material is very easy to work with and can be formed into rings with very little difficulty.

One drawback is that PBI has a useful temperature limit of about 1,040° F. It is chemically resistant, as well as abrasion resistant. The material by itself is quite expensive although this cost is reduced considerably when combined with other materials such as glass fiber.

The last category of material suitable for high-temperature, high-pressure applications are metals. Aluminum has been used and can be used in valves handling HF acid as well as various types of heat-transfer fluids. Aluminum as a packing is normally good to 1,000° F. and can withstand very high pressures. While copper is available, it is rarely used in valve applications. It is still used in certain hot oil reciprocating pumps.

Nickel foil, either wrapped or used in conjunction with inconel mesh, is suitable for very high temperatures in the range 1,800–2,200° F., but movement of the valve stem should be relatively slow, otherwise galling can take place rapidly.

Inconel wires, monel, and stainless steel are typically used as reinforcement in conjunction with the various nonmetallic yarns that we have mentioned previously.

These products are available today to meet refining requirements. Further testing, development, and adaptations of these materials are required to achieve maximum service life, minimum leakage requirements, and total safety.

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# Knowledge is key to stress-corrosion battle

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Of the various forms of corrosion encountered in plants, stress corrosion cracking (SCC) is often the least understood by plant personnel.

Understanding varies from disbelief that SCC can even occur, to fear that all equipment is cracking.

For some mysterious reason, strong, tough, and normally dependable alloys develop cracks and fail. Lack of understanding of stress corrosion leads to the design of installations which are sure to fail.

It allows plant procedures and practices to go unchecked, leading to cracking of equipment. It also leads to frustrating attempts to achieve satisfactory maintenance repair of cracks in vessels and piping.

What is stress corrosion cracking? Why does it occur? What alloys are susceptible? Where might you expect it? What are solutions to the puzzle?

Here is an overview of those issues.

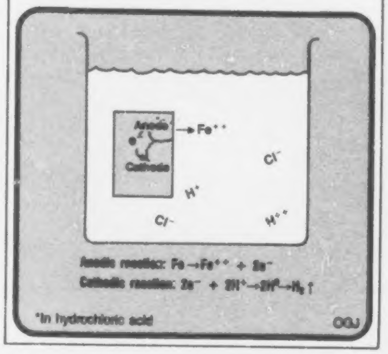
**Review.** First, SCC is a corrosion phenomenon—for it to occur an electrolyte must be present containing a specific ionic species, and there must be tensile stress in the metal. Let's step back for a quick review of corrosion.

Corrosion can be defined in several ways. The corrosion engineer defines it as "the deterioration or destruction of a material through reaction with its environment." Additionally, we might add that corrosion is an electrochemical reaction, requiring the presence of an electrolyte for it to proceed.

To better understand this electrochemical concept, let's take a look at a simple corrosion cell—steel in hydrochloric acid. The acid is a conductive solution (an electrolyte). The piece of steel is made up of many "anodic" and "cathodic" sites (Fig. 1).

Fig. 1

Steel corrosion*


Anodic
Cathodic
$Fe^{++}$
$Cl^-$
$H^+$
$Cl^-$
$H^{++}$
Anodic reaction: $Fe \rightarrow Fe^{++} + 2e^-$
Cathodic reaction: $2e^- + 2H^+ \rightarrow 2H^0 \rightarrow H_2\uparrow$

*In hydrochloric acid

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At the anode, iron is dissolved into the acid in the form of ferrous ions, liberating electrons which pass through the steel to the cathodic sites on the metal surface. At these cathodes, the electrons from the anodic reaction are available to neutralize hydrogen ions in the acid.

The resultant hydrogen atom ($H^0$) then either penetrates the steel or quickly combines with another hydrogen atom to form a molecule of hydrogen gas ($H_2$). Evolution of this hydrogen can be seen when you place steel in hydrochloric acid.

This simplified picture of steel corroding in HCl, i.e., the concept of the anodic reaction and the cathodic reaction is a key concept and will help us understand stress corrosion cracking and make the distinction between SCC and hydrogen-assisted cracking (or hydrogen embrittlement).

The corrosion engineer recognizes that corrosion shows itself in many forms. Traditionally, eight forms of corrosion are recognized.[1] These are:

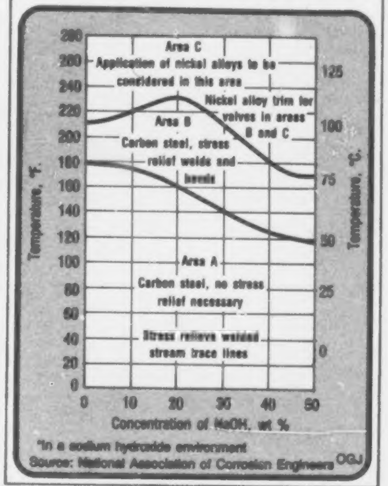
1. General (or uniform) corrosion
2. Galvanic corrosion
3. Pitting
4. Crevice corrosion
5. Intergranular corrosion
6. Selective leaching
7. Erosion corrosion
8. Stress corrosion

These descriptive names evolved during the early years of corrosion science and probably create vivid pictures of problems experienced at all plants. The focus here is on stress corrosion cracking.

**Stress corrosion cracking.** We now know that corrosion is the deterioration or destruction of a material by its environment. We know it is electrochemical in nature. But just what is stress corrosion cracking?

Fig. 2

Steel stress corrosion*



*In a sodium hydroxide environment

Source: National Association of Corrosion Engineers

OGJ

Stress corrosion cracking is defined as the crack initiation and growth in an alloy caused by the simultaneous action of corrosion and tensile stress. This cracking can occur at stresses well below the yield point. The presence of a specific ion/alloy combination is required.

It is generally accepted to be caused by accelerated electrochemical corrosion at local anodic sites on the alloy. It has been demonstrated that it is an anodic phenomenon and can be arrested by application of cathodic protection.[2]

"Everyday" examples of anodic (true) stress corrosion cracking are the cracking of austenitic (300 series) stainless steels by chlorides, the cracking of carbon steel by hot caustic, and the cracking of brass by ammonia solutions.

On the other hand, hydrogen embrittlement, or hydrogen-assisted cracking is caused by ingress of hydrogen into the alloy. The hydrogen comes from the reduction of hydrogen ions at the cathodic sites on the alloy surface.

The hydrogen atoms from these cathodic sites are mobile. Some unite to form hydrogen gas and can be seen as bubbles in the liquid, while others

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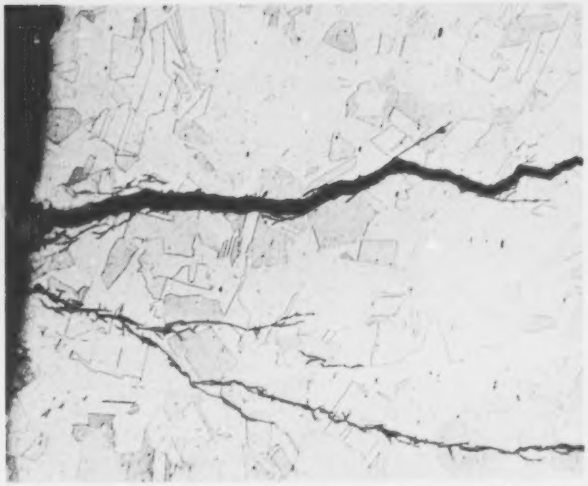
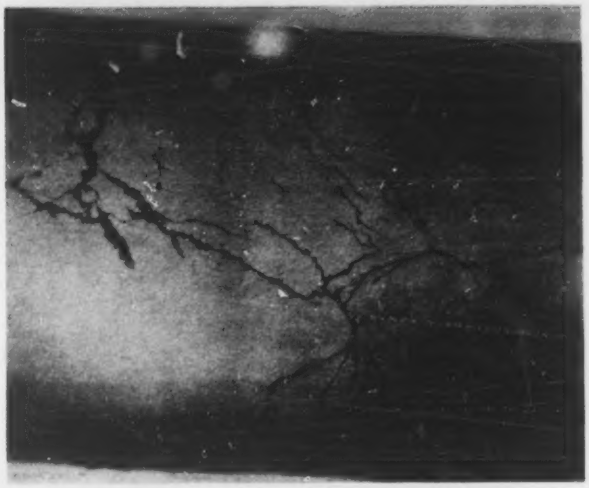
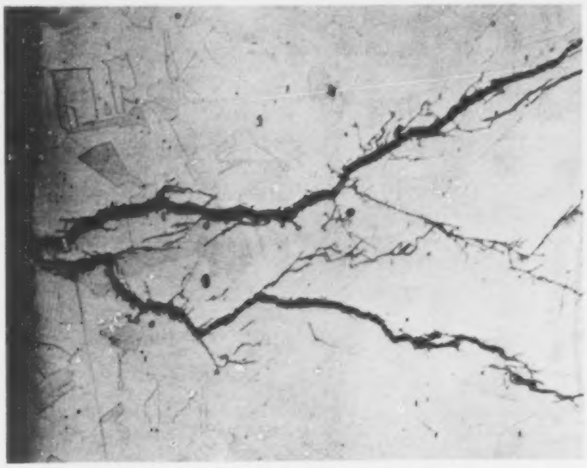
Based on a paper presented at the National Petroleum Refiners Association Refinery and Petrochemical Plant Maintenance Conference, San Antonio, Feb. 18-21.



**Chloride stress corrosion** caused cracks that originated on the inside surface of the pipe (oxalic acid etch, 100×) (Fig. 3).



**Wet, calcium silicate** insulation caused stress corrosion cracks to develop on the outside surface of the pipe (Fig. 4).



**Flooding from heavy rain** caused chloride stress cracking to develop on the outside surface of the pipe (oxalic acid etch, 100×) (Fig. 5).

penetrate into the alloy. Remember, a hydrogen atom is very small and very mobile allowing this penetration to occur.

The hydrogen penetration causes a loss of ductility, resulting in cracking if tensile stresses are present. The susceptibility to this form of attack increases as the hardness (or strength) of the steel increases.

The chemical environment in the liquid affects the rate hydrogen is absorbed. Sulfide, cyanide, and fluoride ions promote the entry of hydrogen into the steel. Since hydrogen is formed at the cathodic sites, you might expect cathodic protection to aggravate hydrogen attack—such is the case and it is easily demonstrated.[3]

**Stress corrosion environments.** Few if any metals or alloys are totally immune to SCC. Table 1 is a summary of some more common alloy/ion combinations which can lead to stress corrosion cracking. Note that this table is far from a complete listing of all such alloy/ion systems, but is presented to give the reader a glimpse of SCC's widespread nature.

While the table identifies systems where SCC can occur, the simple presence of the specific ion does not automatically eliminate the alloy from use. For example, it is wrong to simply conclude that since chlorides can crack austenitic stainless steels, then these stainless steels cannot be used where chlorides are present.

Other variables (primarily temperature, tensile stress, chloride concentration, acidity, presence of oxygen, alloy microstructure) play a major role. Unfortunately, for most systems, the limiting temperatures, stresses, and ion concentrations are ill defined. Experience, judgment, and/or corrosion testing are required to define serviceability of an alloy.

The steel-sodium hydroxide environment is one where published boundaries are available to help the engineer. Data representing industry experience are published by the National Association of Corrosion Engineers (NACE) in their Corrosion Data Survey.[4] Note the chart (Fig. 2) shows a zone of "safe" application of steel (Area A) in the as-welded condition, and a zone where stress relief is needed (Area B). In Area C of the chart, the use of steel is not recommended.

Another environment which causes frequent stress corrosion problems is polythionic acids in austenitic stainless steel. Austenitic stainless steels which have been "sensitized" by heating to 800-1,200° F. are particularly susceptible.

Exposure of these sensitized stainless steels to the polythionic acid environment often leads to rapid failure by intergranular cracking.

The problem is most often encountered in refineries where sulfur and sulfur compounds are present in the process. These oxidizable sulfur compounds react with oxygen and moisture when the units are opened for turnaround.

The oxygen plus moisture combines with the sulfur compounds to form the polythionic acid.[5] Several approaches are used to control this problem. Included are: exclusion of air/moisture entry during shutdown, neutralization washing of equipment before opening for maintenance, and alloy selection. The National Association of Corrosion Engineers Standard RP-01-70 provides added insight into this problem and how to deal with it.

**Stress corrosion prevention.** Prevention of stress corrosion cracking must be a point of major emphasis in the design and operation of our process equipment. There are potential safety, environmental, and cost considerations of an SCC failure, and repair of stress-corrosion-cracked vessels or piping is very difficult to accomplish.

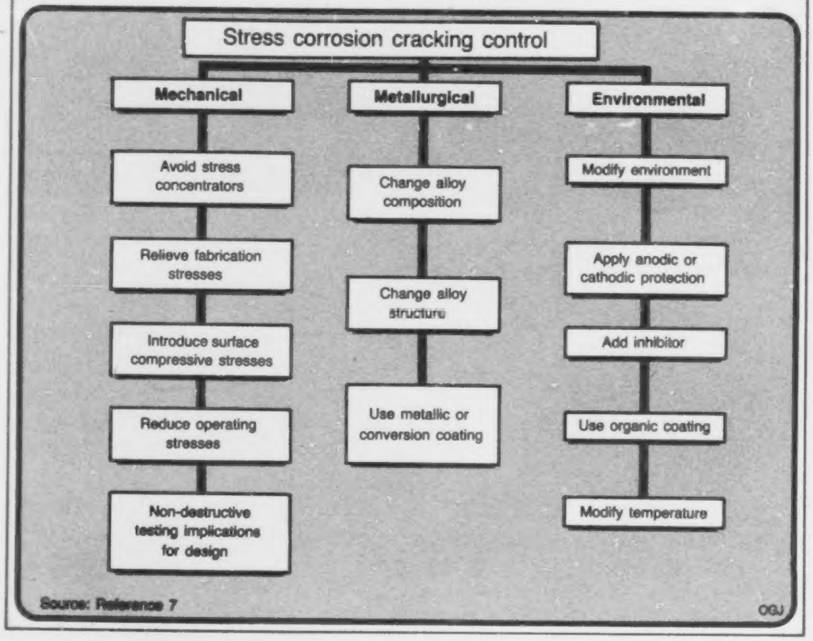
Stress corrosion cracks tend to be highly branched and most difficult to totally remove before beginning a repair weld. The photomicrographs (Figs. 3 and 5) show typical stress corrosion cracks (all are 100×, using an oxalic acid etch).

Any cracking left in the base metal prior to beginning a repair weld will propagate during the heat of welding. Such repair attempts are generally abandoned in favor of replacement of the failed component.

Parkins[7] recently published a paper on stress corrosion control where prevention measures were categorized as mechanical, metallurgical, and environmental (Fig. 6).

Fig. 6

## Stress corrosion control categorized


Stress corrosion cracking control
Mechanical
Metallurgical
Environmental
Avoid stress concentrators
Relieve fabrication stresses
Introduce surface compressive stresses
Reduce operating stresses
Non-destructive testing implications for design
Change alloy composition
Change alloy structure
Use metallic or conversion coating
Modify environment
Apply anodic or cathodic protection
Add inhibitor
Use organic coating
Modify temperature
OGJ

Source: Reference 7

Looking at the Parkins chart, many measures are quite obvious. Most of the "mechanical" and "metallurgical" approaches are measures that must be taken into account during equipment design.

If failures have been experienced with an existing system, these provide possible approaches that can be implemented in a repair or replacement system.

Reduction of tensile stress is the focus of most of the mechanical approaches. Avoidance of stress concentrators is probably insufficient by itself, in most cases, to avoid SCC. It, coupled with thermal stress relief or shot peening, may very well lead to control of SCC.

In a number of situations, reduction of stress through thermal stress relief is sufficient to achieve SCC control. A typical example is stress relief of welds and bends in carbon steel caustic-handling systems.

In some instances, a stress reducion measure coupled with possibly a "metallurgical" or "environmental" control is needed. An example at our plant is a vessel where shot peening to induce surface-compressive stress, coupled with an alloy modification (selection of "L" grade stainless), satisfactorily solved a recurring cracking problem.

The most obvious (and most frequently used) approach for stress corrosion avoidance is through selection of a resistant alloy. The time to "get the alloy right" is during design of a new system.

Unfortunately, our foresight is not always 100%, and an alloy change may be required during a repair or replacement. When a change in alloy is used to correct a stress corrosion failure, be sure the new alloy does not introduce a new and possibly more serious problem (reduced heat transfer, etc.).

"Environmental" stress corrosion controls can often be implemented to correct or avoid a stress corrosion situation. In some instances, the environment can be changed.

Such approaches as painting, use of "dry" closed-cell insulation, and better water proofing are used to tackle stress corrosion cracking of stainless steel pipes and vessels under insulation. These are attempts at changing the crack-causing environment.

Venting the top tube sheet of a vertical heat exchanger with shell side cooling water (Case 8) is a rather straight forward approach at changing the "tidal" zone environment at the top of the exchanger shell to prevent chloride concentration by assuring the tubes stay flooded.

Each stress corrosion cracking problem, or potential problem, should be evaluated to determine the most practical, cost-effective control. A control measure that is effective in one case may be totally ineffective in another.

Similarly, an approach that is cost effective in one situation may be totally prohibitive in another. Following is a summary of 10 "case histories" presented to further exemplify typical stress corrosion problems and applicable solutions.

**Case 1:** Failure of a 3-in., schedule 10S, 304 stainless steel process transfer line.

A new 3-in. line, steam traced and insulated, was hydrostatically tested approximately 4 weeks prior to startup of a new unit. Tracing was placed in service an estimated 7 days before introduction of chemicals.

Plant utility water (50-100 ppm Cl) had been used for the hydrotest. The line was routed from a process unit to tank farm via a "pipe ditch."

Process material was found leaking from the insulation at several locations after the line had been in service 1 week. Removing the insulation, we found that the leak source was fine cracks on the underside of the line, midway between pipe supports.

Failure analysis found that cracking initiated from inside the pipe at locations where residual hydrotest water had been boiled to dryness by the steam tracing. This concentrated the chlorides, causing SCC failure.

Note the highly branched, transgranular cracks characteristic of chloride stress corrosion cracking of austenitic stainless steels (Fig. 3). The cracks initiate on inside surface of the pipe.

**Case 2:** Failure of a 3-in., schedule 10S, 304 stainless steel process transfer line.

The same process line leaked again after 1 year's operation. One of the leakage points was in a section of pipe replaced due to the failure reported in Case 1.

Examination of these failures revealed that the line had failed due to external stress corrosion cracking under wet calcium silicate insulation. The pipe is located in a depressed "pipe ditch," allowing occasional wetting of the insulation during periods of heavy rainfall. The 130° F. process temperature and the steam tracing provided a mechanism for chloride concentration.

The line was stripped of insulation and inspected. Cracked sections were replaced. The replacement piping and remaining portion of the oil line were given a coat of zinc-free silicone paint, and steam tracing was separated from the pipe wall to prevent local hot spots.

Table 1

## Some alloy/ion combinations that lead to stress corrosion cracking

| Alloy | Cracking environment |
|---|---|
| Iron, steel | Caustic (OH⁻)<br>Nitrates ($NO_3$)<br>Monoethanolamine<br>Anhydrous ammonia |
| 300 series stainless | Caustic (OH⁻)<br>Chlorides (Cl⁻)<br>Polythionic acid ($H_2S_4O_6$) |
| Most copper alloys | Ammonia |
| Alloy 400 | HF vapors |
| Titanium | Nitric acid |
|  | Ammonia |

Note the highly branched cracks on the outside surface of the 3-in. pipe in Fig. 4.

**Case 3:** Failure of a 3-in., schedule 10S, 304 stainless steel process transfer line.

The same process line developed numerous leaks again after 5 years' operation! The location of leakage was much like the second failure.

Examination of the line after insulation removal revealed break-down of the paint system and randomly located areas of SCC. Many cracks were not leaking. In most cases, the stainless steel surface had a "rusty" appearance where cracking was present. Insulation was wet at time of its removal.

The third attempt to resurrect this pipe system included inspection, replacement of cracked piping, repainting, separation of steam tracing from pipe wall, and elevation of the line to raise it above flood level of the pipe ditch. This particular section of pipe ditch experienced occasional flooding during periods of heavy rain, and simply painting the line had not provided adequate protection. No further cracking was experienced with the line.

Note the highly branched, transgranular stress corrosion cracks which begin on the outside surface of pipe in Fig. 5.

**Case 4:** Failure to the top tube sheet and tubes of a 304 stainless steel reactor.

Hot (1,200° F.) reaction gas was fed down through the tubes of a vertical 304 stainless steel reactor vessel. The reaction mass was cooled by generation of low-pressure steam.

Steam condensate was fed to the shell side of the vessel and low-pressure steam was withdrawn from the top of the shell.

After 6 years' operation, the unit was forced down due to water leakage into the process. Examination of the reactor found many tubes were leaking and, more seriously, the top tube sheet had cracks which originated at random tube openings.

Removal of the tubes revealed that tubes were stress-corrosion cracked on the water side, with the most frequent incidence of cracking in the crevice between the tube and tube sheet. The tube sheet itself was also cracked, with cracks initiating in the crevice formed between the tube and tube sheet.

Trace quantities of chlorides present in the water were concentrated by evaporation in the crevice between the tubes and tube sheet. Subsequently, both tubes and the tube sheet developed stress corrosion cracks.

The problem was solved by replacing top tube sheet and tube bundle with a high nickel alloy.

**Case 5:** Failure of an alloy 400 hydrofluoric acid (HF) pump-out line.

A 6-in., schedule 10, alloy 400, transfer line was used for occasional transfer of HF from a reactor area to a surge tank. Only two or three transfers to the surge tank were made each year. The line was left contaminated with HF vapors during periods between transfers.

Repeated cracking failures occurred, primarily at the weld heat-effected zones, and in elbows of the 6-in. line. Failure analysis confirmed the cracking mechanism was stress corrosion with cracks initiating on the pipe inside surface due to a moist HF vapor environment.

The problem was solved by flushing the line with a hydrocarbon process fluid after each acid transfer, then leaving the hydrocarbon in the line during periods of inactivity, thus effectively "changing the environment."

**Case 6:** Failure of 304 stainless steel bolts in a cooling tower redwood stairway and handrails.

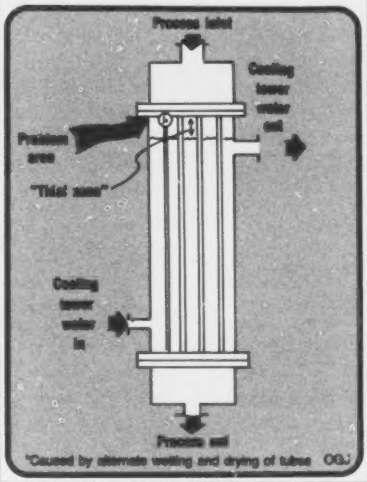
After 12 years' operation, broken bolts were found in the redwood stairway and handrails on a large multicell plant cooling tower. Typically, the bolts were $^3/_8$-in. diameter × 6-in. long, 304 stainless steel hexhead bolts. Metallographic examination of the failed bolts confirmed cracks to be highly branched and transgranular, typical of chloride stress corrosion cracking.

The apparent cracking mechanism was intermittent wetting and drying of the wood which permitted chlorides to concentrate. The Texas summer sun provided sufficent heat for stress corrosion cracking to occur.

The problem was solved by replacement of stairway and handrail bolts with resistant silicone-bronze bolting.

Fig. 7

## SCC failure corrosion*



*Caused by alternate wetting and drying of tubes OGJ

**Case 7:** Failure of 304 stainless steel piping stub ends beneath carbon steel lap-joint flanges.

Leakage developed in 304 stainless steel process piping after 5 years' operation. Investigation found that the leakage source was from beneath carbon steel back-up flanges in the lap-joint flange pipe system. The process temperature was 200° F.

Failure analysis confirmed that stress corrosion cracking originated in the crevice between the steel flange and the stainless pipe. Chlorides from rainwater, washdown water, and adjacent insulation concentrated in the crevice between the flange and piping, leading to the chloride SCC failure. Problem solutions included attempts to coat stainless beneath the carbon steel flange and reduced use of lap-joint flanges in critical, hot-process pipe systems.

**Case 8:** Failure of 316 stainless tubes in a vertical process condenser.

After 5 years' operation, internal leakage developed in a process condenser. The temperature of the process entering the tubes was 200° F. Shell-side cooling water contained 500-1,000-ppm chlorides.

Examination confirmed that classic transgranular stress corrosion cracks originated on the outer wall of the tubes. All cracking occurred at or above the liquid level in the exchanger shell (Fig. 7). Chlorides concentrated in this "tidal" zone where tubes were alternately wetted and dried.

This type of failure has been experienced by many heat exchangers in the chemical process industry.

Traditional approaches to solve the problem include eliminating the use

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of crack-prone austenitic stainless steel tubes in the tidal zone of such exchangers, or elimination of the tidal zone itself. This has been done by venting the shell-side vapor space or exchanger redesign (tube side water/horizontal exchanger/etc.).

**Case 9:** Cracking failure of the top head of a 304 stainless steel reactor vessel.

Examination of the top head of a 230° F. reactor during insulation repair found extensive networks of cracks on the top head. Evidence of process leakage was present at some cracks. The calcium silicate insulation was wet at time of inspection.

Failure analysis confirmed that the cracks were typical branched, transgranular stress corrosion cracks originating on the outside surface of the head beneath the wet thermal insulation. Nuisance leakage of ammonia from the agitator seal, located at the center of the top head, had been continuously flushed with utility water containing 50-100 ppm $C1^-$. The water had wetted the calcium silicate insulation. Chlorides were concentrated on the hot metal surface leading to cracking failure.

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The problem was eliminated by replacement of the head and modifications to the seal to stop leakage. The new head was painted prior to insulation and a closed-cell insulation was selected to lessen the chances of a wet-insulation environment recurring.

**Case 10:** Failure of stud bolts in flanged, internal piping in a hydrofluoric acid process vessel. When the acid settler was opened for routine inspection, it was quite obvious that all stud bolts on internal pipe flanges had cracked. All pipe spools had dropped to the bottom of the vessel.

Examination of the bolts found that they had experienced rather minor corrosion attack. All were cracked. The material of the bolts was confirmed to be A193 grade B7, a high-strength, low-alloy steel which is very susceptible to hydrogen-assisted cracking. These bolts had been installed 2 years earlier.

Failure analysis of the bolts included a metallographic examination and hardness testing. The metallographic exam revealed that cracks were intergranular with some branching. The hardness of the bolts was 29-32 Rockwell C. In light of this evidence, and the nature of the chemicals present, it was concluded that the cracking mechanism was hydrogen-assisted cracking. The bolts were replaced with the correct Monel bolting material and no further problems were experienced.

If plant engineers expand their understanding of corrosion and specifically develop a basic understanding of stress corrosion cracking, they, working with the plant or the company corrosion engineer or metallurgist, can avoid many stress corrosion problems before the problems occur.

Alternately, if a cracking problem has developed, working together, they can define suitable cost-effective control measures to deal with the problem and prevent its recurrence.

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# Catalyst deposits in FCCU power recovery systems can be controlled

**David H. Linden**
Ingersoll-Rand Co.
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Catalyst deposition throughout a fluid catalytic cracking unit (FCCU) power recovery system can lead to significantly higher maintenance costs, operational problems, and even an FCCU outage. The problem of catalyst deposition is an unusual one that is difficult to understand, predict, and eliminate.

Field experience with several power recovery systems, including hot-gas expanders, third-stage separators, and top-pressure control valves, reveals some causes of catalyst deposition, preventions for depositions, and procedures to remove the deposits.

The overall cycle efficiency of the FCC process can be significantly improved by utilizing various waste energy recovery systems such as CO boilers, waste-heat boilers, and power recovery hot-gas expanders. Millions of dollars per year can be saved by the use of these power recovery systems.

But these savings can be significantly reduced by loss of recovery system efficiency caused by deposition of catalyst in the various components that make up the recovery system. Catalyst deposits have been found to occur in the first, second, and third-stage particle separator systems, the process control valves, the power recovery expander, and downstream flue-gas-to-steam boilers.

Although only installations with power recovery expanders (Ingersoll-Rand and four other expander manufacturers) are discussed here, similar depositions are known to occur in FCCU's without power recovery expanders. Fig. 1 shows a typical FCCU power recovery system.

**Component deposition.** The FCCU regenerator usually utilizes two stages of cyclone separators to remove and return the process catalyst overflow to the process for reuse. These particle separators are usually effective in removing 85% of the catalyst overflow from the flue gas.

Deposition in the regenerator cyclones is not normally a problem unless it occurs in the cycle return lines or dip legs. Deposits can plug off the dip legs and prevent the separation of the overflow catalyst. The high catalyst losses resulting from plugging will cause increased operational and maintenance costs as well as increased downstream equipment erosion and deposition. The use of trickle valves on the cyclone discharge minimizes the backflow of flue gas and catalyst but greatly increases the susceptibility of the dip leg deposition and plugging.

A third-stage particle separator is used when a power recovery expander is utilized in the system, or when local environmental regulations limit the flue gas stack particulate loadings. The third-stage separator removes an additional 70-80% of the first two cyclone overflows and leaves an overall separation efficiency of more than 95%.

The third-stage particle separator essentially prevents all particles 10 $\mu$ or larger in size from entering the power recovery expander. The third-stage particle separator usually consists of multiple, small cyclones or swirl vane assemblies.

The separated catalyst is removed from the third-stage separator via an overflow line, using 3% of the flue gas flow to carry the separated catalyst to a final particle separator (such as a fourth-stage classifier or electrostatic precipitator) or to the flue gas stack. Plugging of the individual cyclones, swirl-tube assemblies, or the underflow line with catalyst deposits can lead to downstream equipment erosion or deposit problems.

Unexpectedly, the catalyst deposition occurs in the areas of the highest gas velocities. Catalyst deposits form in the exit holes or discharge slots of the individual cyclones or swirl vanes, and in the critical flow orifice of the underflow line. Deposition can occur rapidly and can be fairly heavy as shown in Fig. 2. There are five major manufacturers of the third-stage particle separators, and all units have experienced deposition and plugging to some extent.

**Expander turbine deposition.** Deposition of catalyst in the hot-gas expander can lead to serious blade wear, power loss, and rotor vibrations. Expander deposition occurs also unexpectedly in the blade path where the gas velocities are at maximum levels.

The most troublesome deposit occurs on the flowpath outer diameter and can build up in thickness until blade tip rubbing and wear occurs. Blade tip wear has exceeded 9 mm (0.375 in.) in some single-stage expanders.

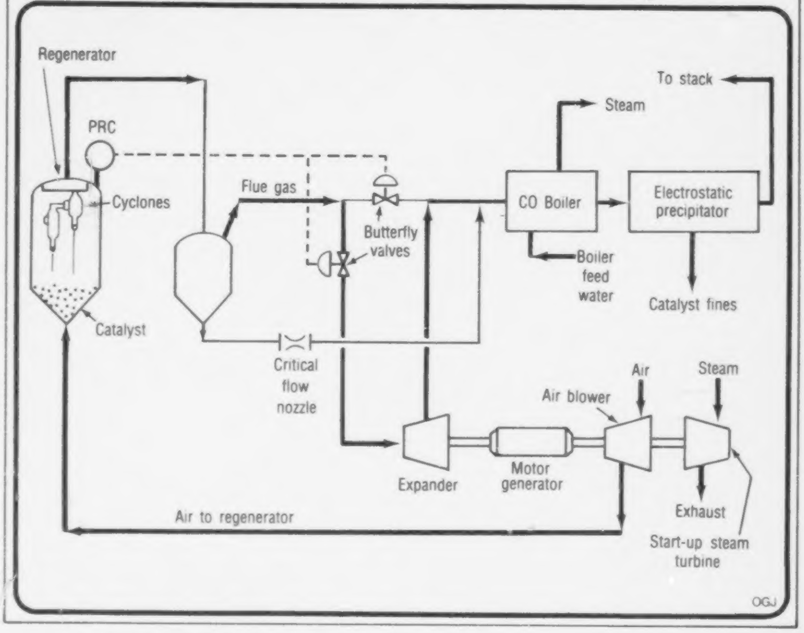
Multiple-stage expanders have been found to be more susceptible to flow path deposition and most particularly, during short-term process upsets. At least three multiple-stage expanders have experienced blade tip wear in excess of 40 mm (1.5 in.).

In each case, deposition occurred on the upstream side of the second and/or third-stage stator. The deposit starts at the outer diameter and builds up in an inward and upstream direction.

Almost all hot-gas expanders experience some minor catalyst deposition which has little or no effect on the expander's performance or reliability. Approximately 20 to 30% of the operating hot-gas expanders experience more significant deposits that may cause significant blade tip wear and some power degradation. One out of ten expanders have experienced major operational problems caused by catalyst deposition. Fig. 3 shows a hot gas expander with very heavy blade-path deposition.

Fig. 1

FCC flue-gas system with power recovery



**CO boiler and precipitator.** Catalyst deposition in downstream boilers can reduce the overall boiler efficiency, promote corrosion, and increase operational and maintenance costs. This same deposition in electrostatic precipitators has led to unit overloading, short circuits, and reduced performance. Again, maintenance and operational costs are affected, and on several occasions, FCCU shutdowns were required.

**Regenerator control valves.** Deposition in the regenerator top pressure control valves has also shown the same unusual pattern of the highest deposition occurring in the valves operating with the highest pressure drop or gas velocities. Bypass valving has been more susceptible to deposits due to the normal mode of operation with full regenerator pressure drop occurring across the valve.

Heavy deposits occur downstream of the seat or disk and have often prevented valve operation. Deposits can collect in the seat areas and cause valve leakage to increase to as much as 15% of the valve full-open-flow capacity.

Fig. 4 shows a section of a heavy deposit that was removed from the seat of a regenerator control valve. This type of deposit will greatly reduce the power of the hot-gas expander and increase the valve wear.

## Catalyst deposits

Catalyst deposit samples from power recovery systems are often very difficult to recover because a process shutdown usually causes the catalyst deposits to break off and carry downstream. The deposits have been retrievable only when the process or equipment is rapidly shutdown or the deposit is of sufficient thickness to prevent its carryover.

The slow shutdown of the FCCU process clears out most of the deposits due to the change in flow conditions, and more importantly, due to the thermal incompatibility of the ceramic deposit to the base material to which it is attached. The catalyst deposit has a thermal coefficient of expansion one-half that of the typically austenitic stainless or alloy steels used throughout the power recovery system. As the structural members cool down, the catalyst deposit is broken up and carried out with the flue gas.

There has been some correlation between the types of catalyst in use and the amount of deposition that has occurred in various FCCU processes. The deposition is usually found in FCC units that tend to be running greatly above the FCC rated capacity (i.e., a 25,000-b/d unit running at 35,000 b/d).

To achieve the higher throughput, process temperatures are increased, air flow is increased, and higher catalyst activity is required. The higher catalyst activity is accomplished by using newer, higher-density and high-activity catalysts, and adding more fresh catalyst. Spent catalyst withdrawal is often used to keep the catalyst activities high.

Catalyst makeup can increase by a

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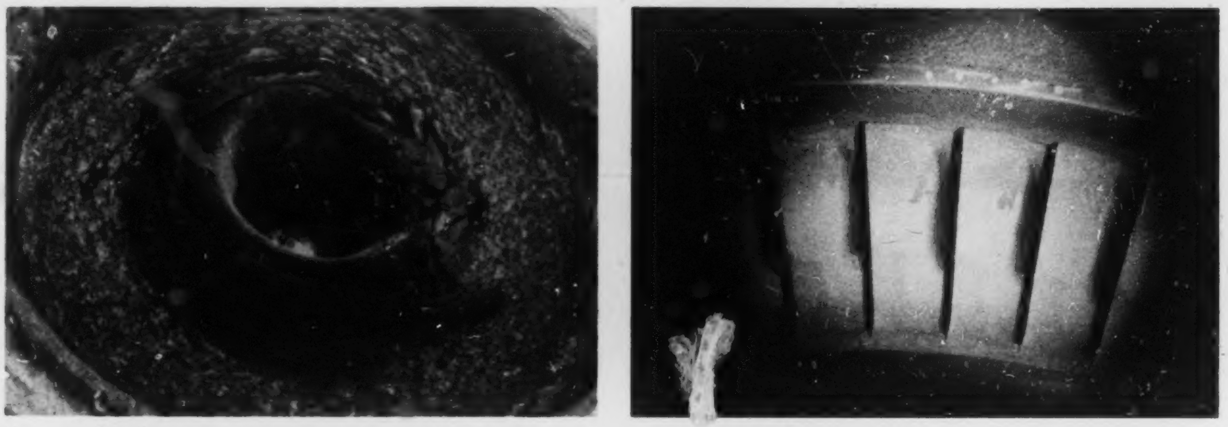
Based on a paper presented at the Katalistiks 1986 FCCU Symposium, Venice, May 12 and 13, 1986.



**Heavy catalyst deposition** (left) occurs in areas of highest gas velocities (Fig. 2). Expander blade path (right) can experience heavy catalyst deposition (Fig. 3).

factor of three or more, and the addition of fresh catalyst always has significant fine particle carryover and loss. As the addition of fresh catalyst increases, so does the fines carryover. Fresh catalyst also has numerous sharp edges and corners that break off and are carried over to the expander. It is these fine catalyst particles (under 5 $\mu$ in size) that deposit in the power recovery systems.

To classify the types of deposition that occur, deposits have been broken down into their various types.

**Deposit Type A.** The first type of catalyst deposit is generally a light, powdery deposit. This type of deposit occurs in areas of low gas velocity and low pressure. It is the most common type of deposit and found throughout every section of the regenerator downstream equipment.

The Type A deposit is generally of little concern except when it occurs in sufficient thicknesses to reduce the thermal efficiency of the waste heat or CO boilers. The Type A deposit occasionally develops very heavily in blanked off sections of pipe and can cause severe catalyst loadings to the downstream equipment when that section of pipe is opened to flue-gas flow.

**Deposit Type B.** The second type of catalyst deposit is generally caused by hydration of the Type A deposit. The normally harmless powdery deposits become very sticky when wet with water.

The most common sources of moisture are from wet steam, water quenches, or condensation that occur during unit start-ups or shutdowns.

The amount of condensation can be greatly reduced by not using any steam in the process until the downstream equipment is warmed up to at least 205° C. (400° F.). The use of flue-gas water quenches should also be eliminated if possible or used only with fine atomizing spray nozzles. At elevated temperatures, catalyst deposition has commonly occurred immediately following afterburns when heavy quenching was used to control the regenerator downstream temperatures.

With operating time, the wet catalyst deposits dry out and become very hard. Often this deposit will have a chalk-like consistency and grayish-white color. The deposit is easily crushed by hand and easily removed from the part it adheres to. This deposit, in general, does not cover large areas and may remain intact through a normal unit shutdown.

If the deposit is fairly fresh, and occurs during a shutdown, the Type B deposit will have a mud-like consistency. On a rapid FCCU start-up, this deposit can be carried downstream and plate out as a splattering. This deposit is commonly found in drain lines and at low points in the system.

**Deposit Type C.** The Type C deposit is commonly found throughout the entire power recovery system, and it is one of the most troublesome deposits. This deposit is very hard and appears to collect in the areas of highest gas velocity, such as the blowdown slots or tubes in third-stage separators as well as separator critical flow orifices, the hot-gas expander flow path, and across the top pressure control valves.

Figs. 2-4 show very heavy Type C deposits. These deposits have been analyzed and have been found to be made up typically of extremely fine catalyst particles; generally, 1 $\mu$ in diameter or smaller.

The deposits are amorphous with no crystalline shape, although they tend to build up in thickness in a columnar shape and in an upstream direction. Fig. 5 shows a microscopic view of a Type C catalyst deposit.

Distinct catalyst particles can be seen adhering together. These deposits can grow to be very thick and exceed 12 mm (0.5 in.) in thickness in less than 6 months of FCCU operation.

Numerous theories of the causes of the deposition have been suggested and include: inertia impaction, particle diffusion, catalyst hydration, electrostatic attraction, magnetism, vapor diffusion, and thermal deposition.

All of these theories exist and may be contributors to the deposition. However, work done by Ingersoll-Rand Cc suggests that the formation of low melting point eutectics may be the true cause. Chemical analyses of these deposits routinely show them to contain very high levels of sodium, calcium, potassium, chlorides, and vanadium.

Measured levels far exceed the levels of typical equilibrium catalyst periodically analyzed by the catalyst manufacturers. The catalyst is often orange in color caused by high levels of iron as well. There is essentially no detectable zeolite remaining in the deposited catalyst, and the aluminum levels are typically lower than equilibrium catalyst.

Examination of the appropriate phase equilibrium diagrams for oxides of the metals or salt compounds indicates that molten compounds are unlikely below 730° C. (1,350° F.). But examination of sodium, potassium, or calcium chlorides shows that low melting point eutectics are probable at low pressures and temperatures between 500 and 650° C. (930-1,200° F.).

These low melting point eutectics make the catalyst very sticky. The common factor in all of the analyzed deposits is the presence of high sodium.

**Deposit Type D.** The last type of deposit found in the power recovery system is one that occurs only in the hot-gas expander. This deposit is actually a transformation of the Type C deposit caused by high temperature and pressure.

The Type C deposit can develop into sufficient thickness to cause expander blade tip rubbing and wear. The rubbing of the blade tips against the shroud can generate enough heat and pressure to sinter or collapse the catalyst deposit into a noncoherent mass without melting it.

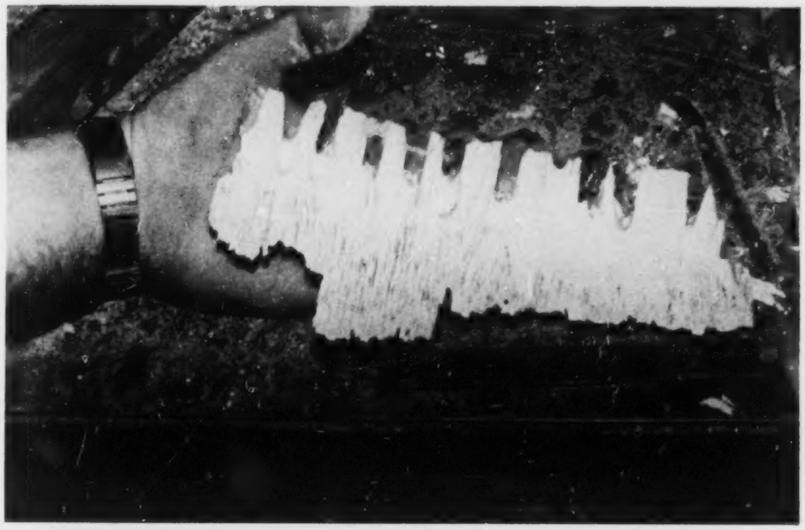
Temperatures in excess of 1,090° C. (2,000° F.) are required to cause this transformation. Evidence of this high local temperature can be seen by examining the rotor blade tips and seeing the metallurgical structural changes.

This type of deposit generally has the same unusual chemistry as the Type C deposit, but with the addition of high levels of nickel or iron from the transfer of blade material. Figs. 5 and 6 show the microscopic differences between the C and D-type deposits. The individual catalyst particles are no longer visible in the Type D deposit.

Deposition in single-stage expanders has caused blade wear predominantly in the midcord region of the airfoil. Fig. 3 shows a severe case of catalyst deposition and blade-tip wear. Several multistage expanders have experienced very heavy Type D deposits in the forward stages, and the deposits caused the heavy wear previously described in this paper.

**Deposit removal.** The removal of the catalyst deposits can be very difficult depending upon the location and the type of catalyst deposit. The Type A deposit is of little concern and can be removed by cleaning procedures (outlined later) or by a brisk sweeping during a unit shutdown. Often the Type A deposit will be removed during normal FCCU operation.

The Type B deposit is of some concern because, if it is left alone, the deposit can be baked onto the attached part during further operation. This can be the start of the more serious depositions.



**Regenerator control valve** seat deposits increase seat wear and valve leakage (Fig. 4).

Catalyst deposits often contain significant amounts of heavy metals or salts that can lead to high temperature crevice corrosion. Fortunately, the Type B deposit is usually swept away by normal operation where flue gas velocities are above 45 mps.

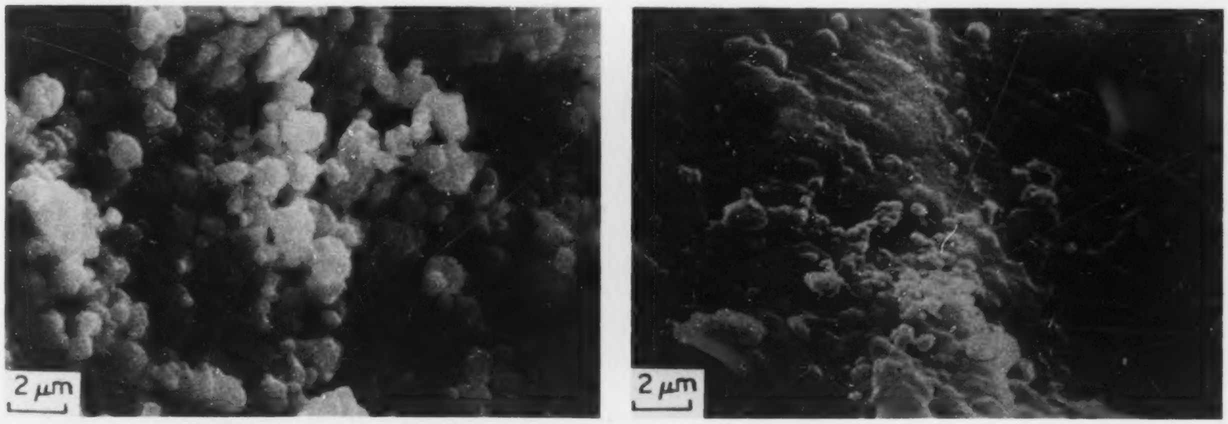
Lower boiler velocities may not be sufficient to remove this deposit from the boiler tubes, and this can affect the unit's efficiency. Some FCCU operators have found that aggressive online cleaning techniques, such as the injection of abrasive cleaning materials, are effective in removing these boiler deposits.

The more adherent catalyst deposits (Types C and D) have shown unusual behavior. These deposits are present during normal operation, but tend to remove themselves during a normal FCCU shutdown. The deposit is removed during a normal slow shutdown where the unit cool down is slow, i.e., 220° C./hr (400° F./hr) or less.

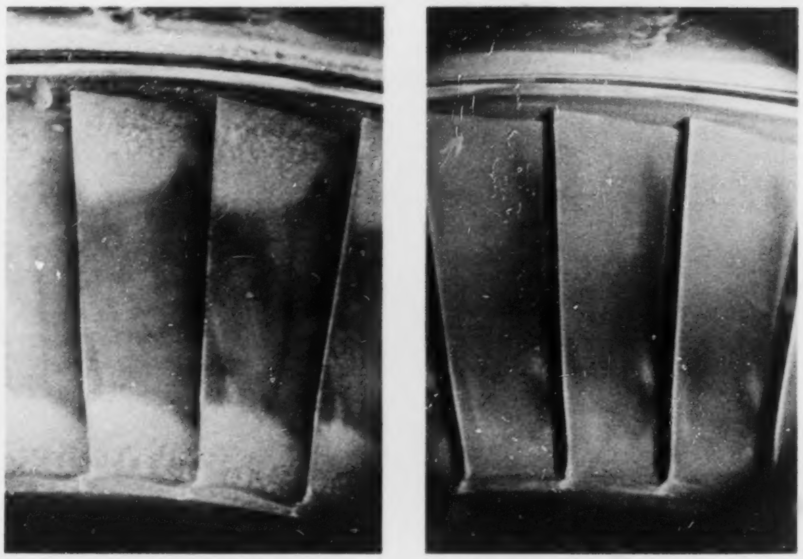
The deposits are removed because of the large thermal growth differences that exist between the ceramic-like catalyst deposit and the typically used austenitic stainless steel or alloy steel duct work and casings. The large dimensional changes that occur during the cooldown makes it difficult for the deposit to adhere to its attached structure.

Conversely, a rapid shutdown of the process may not allow the deposit to dislodge and be carried downstream. There have been occurrences where hot-gas expander rotors have locked up and were unable to be restarted due to catalyst deposits jammed between the blade tips and flow path inner diameter. Similarly, numerous regenerator top pressure control valves have been locked up due to catalyst deposits lodging in the shaft/disk seal area.

As previously described, the C and D-type deposits can cause, in power



**Amorphous, noncrystalline** deposits (left) tend to build up in thickness in a columnar shape, and in an upstream direction (Fig. 5). High temperature and pressure transforms deposit (right) into one where the individual catalyst particles are no longer visible (Fig. 6).



**Cleaning procedure** can effectively remove these types of deposits (left) on expander blades (Fig. 7). Expander blades (right) cleaned by procedure (Fig. 8).

recovery expanders, significant blade wear, a loss in efficiency, and high vibration; in third-stage separators, plugging; in boilers, a loss in efficiency and wear; and general valve operational problems. On-line catalyst cleaning would greatly reduce operational and maintenance problems and maximize FCCU throughput.

## Cleaning procedures

Three on-line deposit-cleaning procedures have been found to be effective in removing the various power recovery system deposits.

**Thermal cycle/reduced production.** This procedure was the first successful on-line cleaning procedure and is based on the observation that most catalyst deposits were removed during a normal unit shutdown. Often an FCCU unit was shutdown because of catalyst deposit problems only to find that deposits were not present after shutdown, and a unit restart would go successfully. The procedure has been successfully used dozens of times in at least nine expander installations that the author is aware of, and with nearly a 100% success rate:

1. Prepare the FCCU for a normal shutdown.

2. Cut back the reactor feedrate in approximately 20% increments while maintaining as high an air rate as possible. The reduced coke makeup and the excess air flow will reduce the regenerator discharge temperature.

3. Continue to reduce the feed rate in similar increments while maintaining the air rate as high as possible for stable regenerator operation until the regenerator discharge temperature drops by 220° C. (425° F.). The total process throughput reduction is variable and dependent upon unit size, volumes, flow velocities, etc.

The rate of temperature change should not exceed 111° C. (230° F.) / hr. (Note: The greater the feed rate reduction, the faster the regenerator temperature will drop.) Experience has shown that a temperature drop in excess of 250° C. (480° F.) has had no additional benefit in removing the deposits, and causes unnecessary temperature cycling of equipment.

4. Hold the reduced operating temperature for at least 1 hr. Deposit removal can be monitored through the expander view ports.

5. Return the FCCU process to full operation at a heat-up rate not to exceed 220° C. (425° F.)/hr.

This procedure is at a very low risk to upsetting the process and downstream equipment while having a very high success rate.

Too rapid a cool down or not reducing the temperature sufficiently are the only reasons for the procedure to be unsuccessful.

**Thermal cycle/full production.** Many FCCU power recovery systems utilize a full or substantial capacity expander bypass system. This second clean out procedure allows the cleaning of the power recovery expander and regenerator top pressure control valves, but does not cover the regenerator cyclones, third-stage separator, or waste-heat boilers. The procedure thermally cycles the power recovery expander and fully strokes the control valving:

1. Switch the expander inlet valve control from automatic to manual. Be sure the bypass valves remain in automatic or be prepared to stroke the bypass valve in unison with the inlet valve to prevent regenerator pressure fluctuations.

2. Slowly close the expander inlet valve from its original position to the fully closed position. To minimize regenerator pressure fluctuations, the inlet valve closure should be done over a 10-20 min time period. This is ample time for bypass valve tracking.

3. The inlet temperature to the expander will drop during the next several hours. The magnitude of the temperature drop will be dependent upon the inlet valve leakage or closure area on valves with stops or parts, piping insulation, and flue gas temperature quenches.

4. A 220° C. (425° F.) temperature drop is required for the most effective catalyst removal.

5. After holding the reduced inlet temperature for 1 hr, reload the expander in the reverse procedure. The expander exhaust temperature should be monitored so that the maximum levels are not exceeded. This is best done by quickly loading the expander to a minimum pressure ratio of 1.3.

The desired temperature drop may not be achievable because of reduced bypass capability, inlet valve minimum flows, low piping heat losses, etc. In these cases, users have had to use steam, water, or air quenching to help lower the flue gas temperature. Some installations have designed or modified the existing piping systems to accommodate this requirement.

Figs. 7 and 8 show a typical hot-gas expander that has been thermally cleaned.

Any flue gas quenching should be done as far upstream of the expander as possible. Do not use the expander internal cooling systems to cool the flue gas because this does not cool the appropriate catalyst-coated blade path components and can actually cause expander vibration and distortion.

This thermal cleaning procedure has worked successfully in several installations, but it is limited to which power recovery system components it cleans and may not be applicable to units with low or no bypass capability.

**Walnut shell cleaning.** The last on-line catalyst deposit cleaning procedure utilizes the injection of walnut shells into the inlet of the expander. This procedure is new, has had limited application, and is effective in cleaning the hot-gas expander only.

The procedure may be applicable to other equipment in the power recovery system. Close monitoring of the power recovery system is important since the walnut shells are most effective in cleaning the A, B, and C-type deposits. With close monitoring, the formation of the D-type deposit

## The author. . .

**Linden**

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can be prevented.

Caution: Injection of foreign material into any piece of equipment poses some risk. The original equipment manufacturer should be consulted for the relevant injection parameters before any cleaning procedure is attempted.

### Deposit reduction steps

The following courses of action have been effective in reducing the amount of, or even eliminating, the deposition of catalyst in the power recovery systems:

1. Proper sizing, operation, and maintenance of the three stages of particle separation to control catalyst erosion and deposition
2. Upgrading of older separator designs to newer more efficient designs
3. Using higher amounts (greater than 3%) of flue gas underflow from the third-stage separator
4. Using long radius elbows on the third-stage separator underflow lines and equipping the elbows with cleanout valves that allow online cleaning (rodding)
5. Instrumenting the third-stage separator underflow lines to detect flow reductions from blockage
6. Minimizing or eliminating the use of steam or water quench systems and the purging of piping expansion joints
7. Using superheated steam and water atomizing nozzles when quenching or purging is required
8. Using quenching and purging only when the power recovery system temperatures are above 205° C. (400° F.) to prevent condensation
9. Selecting the catalyst type to minimize deposition rates
10. Minimizing catalyst contaminents such as heavy metals or salts
11. Minimizing thermal gradients wherever possible
12. Designing for aerodynamically smooth flow passages to eliminate flow interruptions and stagnation areas
13. Providing smooth flow paths that do not allow the catalyst a place to stick
14. Monitoring catalyst deposits while in service through devices like expander viewports
15. Cleaning deposits out before the more detrimental catalyst deposits can develop

Up-front system design, analysis, and operational procedures can often reduce or eliminate catalyst deposition. On-line monitoring and periodic cleaning can prevent existing deposition from becoming a problem.

The types and causes of catalyst deposition are numerous and difficult to understand. Further research and informational exchanges will be required to totally eliminate this FCCU operational problem. A joint effort and informational exchange by catalyst manufacturers, process designers, contractors, original equipment manufacturers, and users is greatly encouraged.

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# Tower packings cut olefin-plant energy needs

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Replacing trays with metal tower packings in ethylene plant hot-section towers results in significant pressure drop reductions.[1] Major ethylene producers are applying this technology to achieve various process improvements.

At E.I. du Pont de Nemours & Co.'s Sabine River works (Texas) ethylene plant, tower packing was installed in the top section of the water quench tower (Fig. 1) to reduce energy requirements and improve ethylene yield. The 89% lower pressure drop of the packed section, compared to that of the trays replaced, was utilized to reduce the load on the cracked-gas compressor and improve selectivity. The actual ratio of compressor horsepower savings to furnace selectivity savings depends upon the relative cost of products and feedstocks.

At Union Carbide Corp.'s Taft, La., plant, low-efficiency contactors in the bottom section of the water-quench tower were replaced with metal tower packing in order to improve the heat transfer efficiency.

The purpose of the revamp was to increase the bottom effluent temperature without sacrificing the top temperature approach. The hotter liquid effluent eliminated the need for auxiliary low-pressure steam which was required in another area of the plant.

**Du Pont plant.** The ethylene unit at Du Pont's Sabine River works in Orange, Tex., was started up in 1969. The plant is designed for feedstocks between 50:50 and 95:5 ethane-to-propane ratios. The plant originally was rated for an ethylene capacity of 750 million lb/year, but currently is rated at 850 million lb/year. The products are ethylene, propylene, a mixed $C_4$ stream, and a $C_5+$ aromatic distillate.

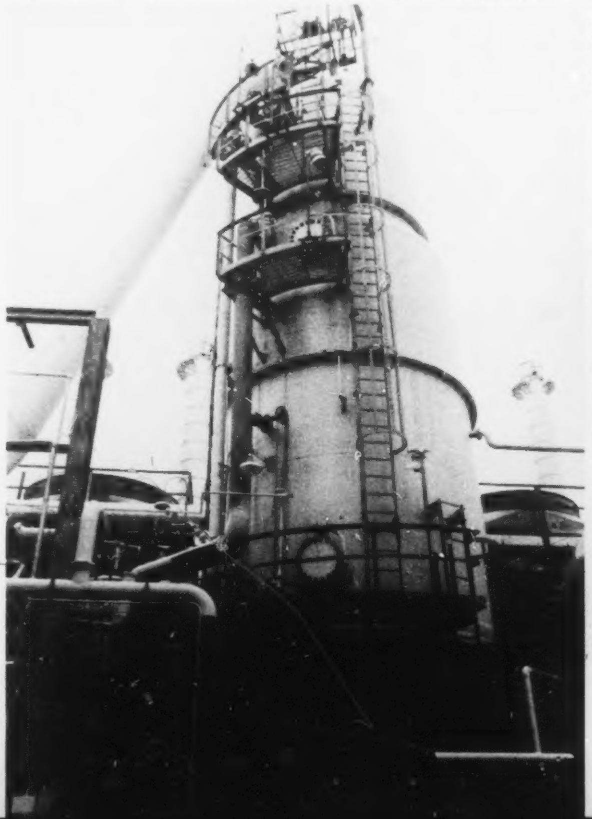
The hot section (Fig. 2) consists of the cracking furnaces, heat removal, gas compression, acid gas removal, and gas drying subsections. The cracked gases leave the cracking furnaces at 850° C. and initially are cooled to 180° C. by heat recovery exchangers which produce steam.

This gas then enters the quench tower where the gas is cooled to 35° C. by contact with recirculated water in two sections. The top section contained valve trays prior to revamp and the lower section angle-iron decks.

Dilution steam and higher-molecular-weight by-products condense in the water-quench tower. The organic by-products are decanted in the quench settler and removed for further processing. Savings from a reduction in pressure drop in the hot section can be obtained in two ways. Furnace pressure can be held constant and the pressure reduction will result in a higher compressor suction pressure. This reduces the compressor horsepower requirements.

The equation for compressor horsepower requirement can be written:

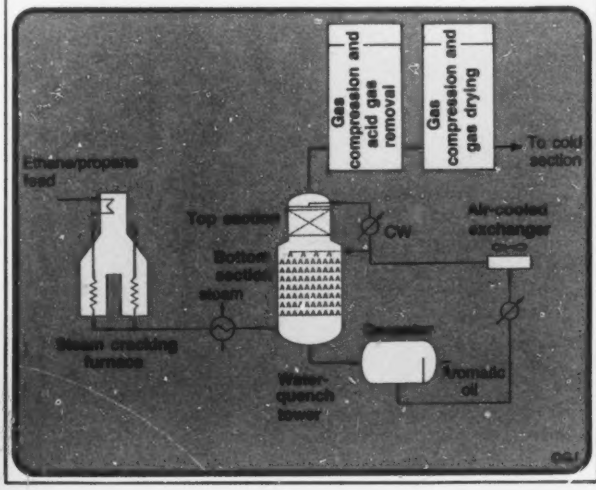
$$P = \frac{W}{E_A}\left[\frac{k}{k-1} \times ZRT_o\left(\frac{P_i}{P_o}^{(k-1)/k} - 1\right)\right]$$



**Packing was installed** in the top section of this water quench tower at Du Pont's Sabine River works (Fig. 1).

Fig. 2

Du Pont hot section flow diagram



**Quench tower packing size** was chosen to optimize heat-transfer efficiency and minimize pressure drop (Fig. 3).

**Ladder-type pipe distributor** spreads liquid uniformly over the packing by means of metering orifices (Fig. 4).

where k is the ratio of the heat capacity of the gas at constant pressure to the heat capacity at constant volume, P is the power requirement, W is the mass flowrate, $E_A$ is the adiabatic efficiency, and the subscripts "o" and "f" denote initial and final conditions. R is the universal gas constant, and Z is the gas compressibility.

It can be seen from this equation that an increase in $P_o$ at a constant $P_f$ reduces the power requirements.

Alternately, the furnace pressure can be lowered at a constant compressor suction pressure to improve furnace selectivity to desired olefins and increase the product yield by lowering the hydrocarbon partial pressure.[2]

The relative value of energy vs. feedstock costs determine the optimum operating strategy.

When preliminary studies on packing the quench tower were done, the greatest cost savings could be obtained from improved selectivity. At the time the packing was installed, however, the greatest savings could be obtained with higher suction pressure on the compressor.

The economic data presented are based on energy savings; however, current feedstock prices again favor lower furnace pressures for improved selectivity.

**Original unit.** The quench tower was originally built with seven angle-iron decks in the 16.5-ft ID bottom section. The 13.5-ft ID top section contained six valve trays on 24-in. spacings.

Quench-water flow to the distributor above the top section is in excess of 1 million lb/hr at a temperature of 35° C. The pressure drop through the tower ranged from 0.8 to 1.4 psi. Indicated top temperature approaches (exit gas temperature minus top inlet water temperature) typically varied between 1.5 to 5.5° C., depending on the season.

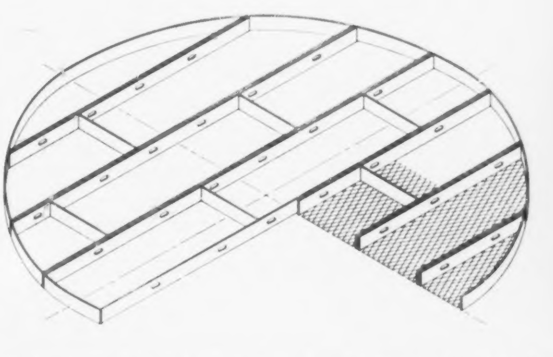
Quench-water-flow rates to the tower are not controlled. Maximum flows are maintained and manual valves adjusted to control the relative heat removal between the top and bottom sections. Cracked hydrocarbon gas and steam are fed to the base of the tower. The inlet combined vapor temperature is 180 to 190° C.

**Evaluation.** Because the majority of the pressure drop in the water quench tower (90%) was from the valve trays in the top section, it was decided to replace these trays with packing.

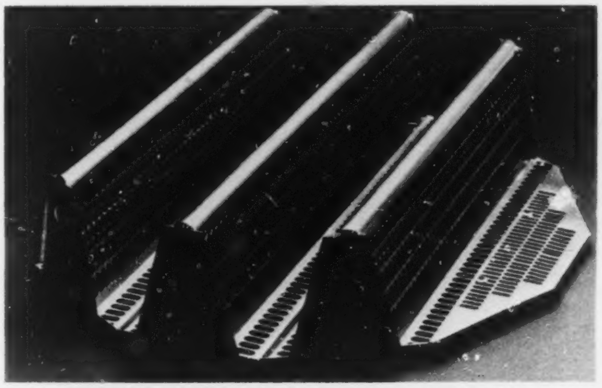
Two types of packing were evaluated. Norton Co. provided data on its proprietary, high performance IMTP packing. Quotations and performance data were also obtained on Pall rings.

Pall rings were lower in cost, but would not provide as much pressure drop reduction. Bare equipment costs of the IMTP packing and engineered internals were somewhat greater but yielded a predicted additional cost savings of $6,500/year. IMTP metal tower packing was selected on the anticipated higher savings and based on Norton Co.'s experience with similar quench tower installations.

**Installation.** The six valve trays in the top section of the water-quench tower were replaced with a 9.25-ft deep bed of No. 50 IMTP tower packing. A detail of this packing is shown in Fig. 3.



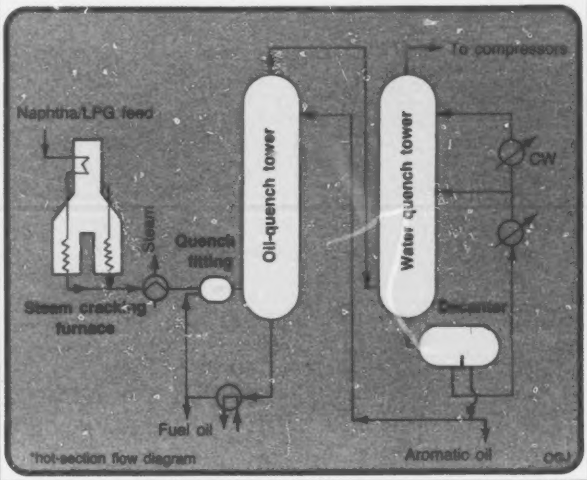
**Bed limiter** keeps the packing elements from shifting in top of the bed (Fig. 5).



**Gas-injection support plate** holds the weight of the packing and the liquid holdup in the bed (Fig. 6).

Fig. 7

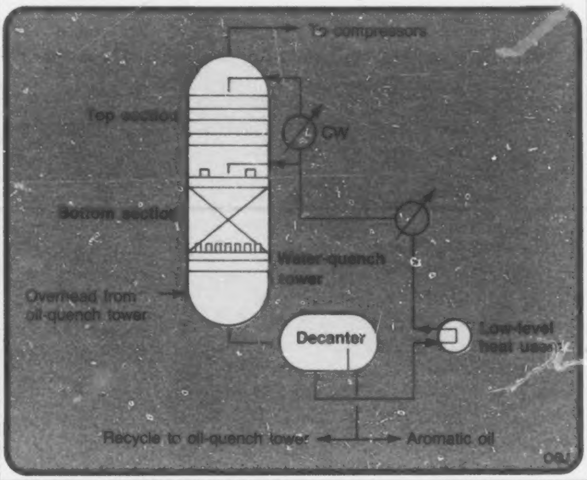
Typical naphtha fed ethylene plant*



*hot-section flow diagram

Fig. 8

Union Carbide water-quench tower



The packing size was chosen to optimize the heat transfer efficiency and minimize the pressure drop at the expected loadings. The internals supplied included a liquid distributor (Fig. 4).

The top quench water is pumped to the main header and distributed to the laterals. This is a ladder-type pipe distributor that operates by distributing liquid uniformly over the packing by means of metering orifices.

The noninterfering bed limiter keeps the packing elements from shifting in top of the bed (Fig. 5). It is retained by the support system of the distributor.

The gas injection support plate holds the weight of the packing and the liquid holdup in the bed (Fig. 6). This type of packing support plate usually has a larger free area than the tower cross section. This plate is designed to provide separate flow space for the vapor and liquid and operates at a negligible hydrostatic head.

Stainless steel was chosen for the liquid distributor since corrosion could not be tolerated in the orifices without adversely affecting distribution. Carbon steel was selected for the packing and support plate.

The circulating quench water has a pH of 4-5 and corrosion of carbon steel would be expected. However, oils produced as cracking byproducts, that are present in the quench water, coat metal surfaces and reduce corrosion. Measured corrosion rates in the quench system are quite low.

Revamping of the existing tower presented several installation concerns. Burning or welding in the tower would be unsafe without completely cleaning all oil and tar from the tower. The liquid distributor and packing support plate were modified to permit bolting to existing tray support rings.

Burning was not completely eliminated by design changes. Four downcomer support brackets were removed from the tower walls to permit proper installation of the packing bed limiter. The first two trays were removed, the top section hydroblasted, and tarps installed over the third tray. By flooding the tarps with water and monitoring the explosivity, the brackets were safely cut from the tower.

The tray support rings were left in place. The bottom tray ring was completed using bolt-in sections to accomodate the packing support plate.

When water flow was established after the packing installation was completed, the ladder-type distributor partially plugged in 3 days. The distributor was removed and cleaned. Less than 1 lb of solid material was present, but over 80% of the orifices were plugged.

External quench water piping was modified to permit installation of dual in-line Y strainers. These strainers can be backflushed and steamed for online cleaning.

The strainers, which have 1/64-in. openings, are switched every 3 to 4 days. To further reduce the chance of fouling, the distributor orifice sizes were increased slightly. Since these modifications, the distributor has shown no signs of plugging in the 1 year since installation.

Fouling of distributors from particulates present in process streams should be carefully evaluated. Although packing has more open area than trays, and is less likely to foul, orifice-type distributors must be kept free of fouling material in order to assure optimum performance.

**Results.** The data for the tower are monitored continuously and stored for graphical recall on a computer. Summer operating data taken before and after the revamp are detailed in Table 1.

For the trayed tower, the pressure drop through the valve trays averaged 37 in. of water. The packed column, under similar conditions, shows a recorded pressure drop of 4 in. of water.

This indicates an 89% pressure drop reduction in the top section using No. 50 IMTP packing. Recorded data indicate a pressure drop reduction in the whole tower of 0.8 to 1.2 psi. The top temperature approach was also improved.

**Economics.** Total costs included $60,000 for internals and packing installation and $35,000 for the external piping modifications required for the addition of strainers. Annual savings are $105,000 based on a weighted average pressure drop reduction.

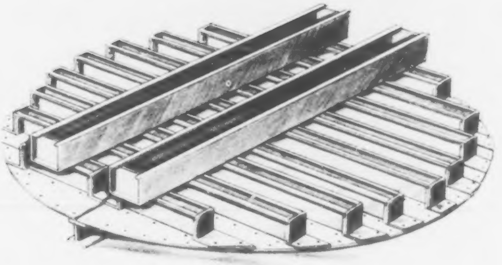
**Union Carbide plant.** Union Carbide utilized packing in a water-quench tower for a different reason in its Taft, La., ethylene plant.

The reported feedstocks are liquified petroleum gas and naphtha.

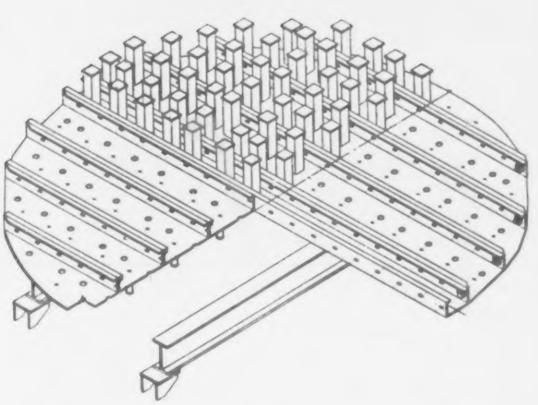
Because of the relatively low conversion of these feedstocks to ethylene, and the large amount of high-molecular-weight hydrocarbons in the cracked gas in this type of plant, the hot section also includes an oil quench column (primary fractionator) (Fig. 7).

The purpose of this tower is to cool the gas to slightly above the water dew point and to condense heavy fuel oil. The overhead vapor from the oil quench column then enters the water-quench tower at approximately 95° C.

**Evaluation.** Prior to revamping, the water quench tower contained several conventional-type trays in the top irrigated section and low-efficiency con-



**Orifice plate** liquid distributor replaced chimney tray (Fig. 9).



**High $F_S$ factor** of the inlet vapor required the use of a gas-distributing support plate (Fig. 10).

tactors in the bottom section. A chimney tray for distribution of water separated the two sections.

The pumparound water temperatures vary significantly depending on the season. The overhead vapor temperature was maintained at approximately 25° C. in winter and 33° C. in summer.

Prior to this project, the water-quench tower operated with base temperatures ranging from 60 to 65° C. Additional low-pressure steam was required to raise the temperature of this stream to 80° C. in summer and 75° C. in winter to satisfy heating requirements elsewhere in the plant. There was significant justification, therefore, in revamping the water quench tower to eliminate the need for auxiliary steam requirements.

The goal of this revamp was to raise the bottom water temperature. By replacing low efficiency contactors with the more efficient metal tower packing, the heat transferred from the cracked gas stream in the bottom section of the water quench tower is increased. This raises the bottom water temperature and reduces the heat load in the top section of the column.

Table 1

## Du Pont's quench tower operating data

| | Trayed (9/84) | Packed (9/85) |
|---|---|---|
| **Rates, lb/hr** | | |
| Vapor feed | Base | 1.15 × Base |
| Water to top of column | 970,000 | 1,120,400 |
| Water to middle of column | 1,400,000 | 1,652,800 |
| **Temperature, °C.** | | |
| Vapor feed | 190 | 191.9 |
| Water to top of column | 34 | 36.2 |
| Water to middle of column | 55 | 51.2 |
| Top vapor product | 36.6 | 36.8 |
| Bottom liquid to decanter | 78 | 74 |
| Top temperature approach | 2.6 | 0.6 |
| **Pressure, psig** | | |
| Top of column | 15.0 | 15.32 |
| Below top section | 16.34 | 15.46 |
| Bottom of column | 16.45 | 15.57 |
| Total tower pressure drop | 1.45<br>(40 in. of water) | 0.25<br>(7 in. of water) |

In order to achieve the desired results, the upper two-thirds of the low-efficiency contactors, in the lower section, were replaced with an 11½-ft-deep bed of No. 50 IMTP packing as is shown in Fig. 8. The chimney tray was replaced with an orifice plate liquid distributor/redistributor (Fig. 9).

Modified parting boxes were used to collect liquid from the valve trays and to feed the distributor/redistributor. A noninterfering bed limiter was used on top of the packed bed (Fig. 5), and a gas distributing support plate was used to support the packed bed.

The use of the gas-distributing supporting plate (Fig. 10) was required due to the high $F_s$ (vapor capacity factor) of the inlet vapor. The $F_s$ term is a measure of the kinetic energy of the inlet vapor stream and, depending on its magnitude and the pressure drop in the packed bed, determines whether or not a gas distributing support plate is required. For the revamp, this plate was designed to have a maximum pressure drop of 4 in. of water.

**Results.** After installation of the

**Results.** After installation of the

IMTP system, the operation of the column was improved dramatically. At summer conditions, the water quench tower operated at an 80° C. base temperature, and the top approach was maintained. At winter conditions, when colder process water was used, the column operated at 74-75° C. base temperatures and an overhead vapor temperature of 25° C.

**Economics.** The installed cost was $207,000. The plant saved $300,000/year by eliminating the low-pressure steam requirements which had been required in another area of the plant.

The overall pressure drop of the column was increased by 2 to 3 in. of water, due mostly to the gas distributing support plate. This was not considered as a significant penalty. The water-quench tower has been in operation for over 1 year without pressure drop increases or efficiency losses.

**Summary.** These two installations have demonstrated how metal tower packings can be used in ethane/propane and naphtha-fed ethylene plant water-quench towers to achieve significant cost savings. In these two

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Other responsibilities include developing design procedures, trouble shooting, data analysis, and sales support. Prior to joining Norton in 1983, Sauter did graduate level research work in heterogeneous catalysis. He has a BS in chemical engineering from the University of Akron and he is a member of AIChE.

William E. (Bud) Younts is production supervisor of the high density polyethylene manufacturing unit at E.I. du Pont de Nemours & Co.'s Sabine River works in Orange, Tex. He has had previous assignments with the plant technical ~~services~~ and process development.

Younts received a BS in chemical engineering from North Carolina State University and he is a member of AIChE.

instances, IMTP systems were chosen due to the critical requirements of pressure drop reduction and thermal efficiency. In the Du Pont plant, packing the top section of the water-quench tower reduced the pressure drop in the top of the tower by 89% with an improved temperature approach. In the Union Carbide plant, the effluent water temperature was increased by an average of 15° C. (summer).

The economic benefits in both cases justified these projects.

### Acknowledgments

The authors gratefully acknowledge the cooperation and permission of E.I. du Pont de Nemours & Co. for providing operating data on its Sabine River works plant operation and the Union Carbide Corp. for allowing the inclusion of performance results on the operation of the water quench tower at its Taft, La., plant.

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# New correlations predict FCC feed characterizing parameters

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New correlations have been developed by Total that accurately predict the important fluid catalytic cracking (FCC) feedstock characterizing parameters: aromatic carbon content, hydrogen content, and molecular weight.

The correlations are utilized in Total's FCCU model which operates in conjunction with a non-linear optimizer.

The refractive index, an important measure of feedstock quality, can also be estimated by the Total correlations.

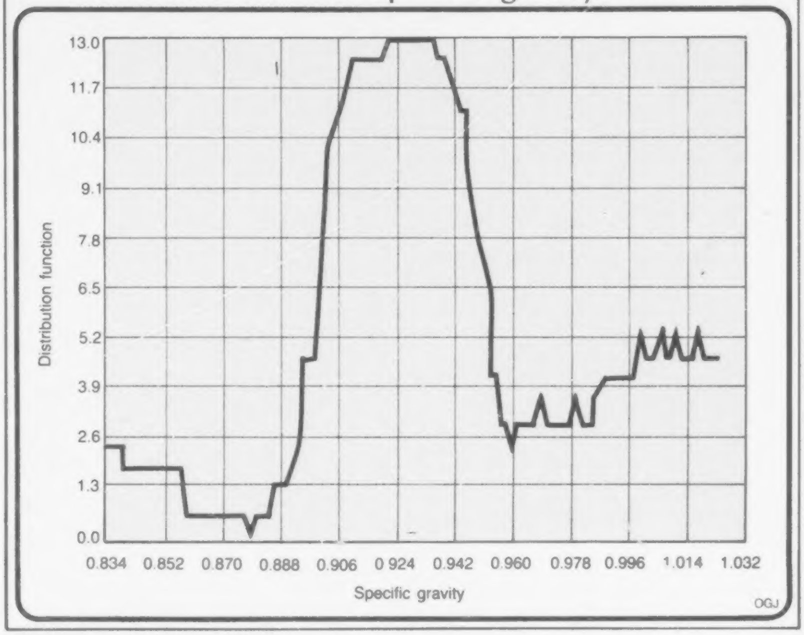
The characterization of fluid catalytic cracking (FCC) feedstocks is very important for modeling the FCCU as well as the FCCU design and operation. Since the complete composition of FCC feedstocks cannot be easily established on a routine basis, the composition is lumped into the different species such as aromatic carbon, napthenic carbon, paraffinic carbon, hydrogen, sulfur, etc. This lumped composition generally serves as the input for a model of the FCCU or correlations of its design.

An ultimate goal of characterization of FCC feedstocks is to relate the feed quality to product yields and qualities for a particular set of operating conditions. Many methods have been suggested in the literature for characterization of petroleum feedstocks. Some of them use only the API gravity and Watson, UOP K factor which are not adequate to characterize the complex FCC feedstocks.

Some methods employ sophisticated analytical techniques such as liquid/gas chromatography, mass spectrometry, nuclear magnetic resonance (NMR), etc. These complex tech-

Fig. 1

Normal distribution of specific gravity data



niques are neither available nor convenient to use in a refinery for a daily operation.

The characterization method used in the TOTAL model of the FCCU requires the usual laboratory tests carried out in a refinery on a daily basis. These tests are:

- Specific gravity at 15° C.
- Refractive index and the temperature at which it is measured
- Sulfur content
- Basic nitrogen content
- Conradson carbon content
- Metal contents (nickel and vanadium)
- Viscosity at 37.8° and 98.9° C.
- ASTM D1160 distillation

The new correlations are incorporated in the total yields and properties prediction model of the FCCU to estimate the aromatic carbon content, hydrogen content, molecular weight and refractive index using the above usual laboratory tests are described. The evaluation of the existing and the new total correlations is also given.

**Feedstock data.** In order to develop the correlations, 33 different FCC feedstocks were selected having the following variations of analysis parameters:

| | |
|---|---|
| Specific gravity at 15° C. | 0.8335-1.0133 |
| Refractive index at 60° C., | 1.4459-1.5681 |
| Sulfur content, wt % | 0.14-4.50 |
| Conradson carbon, wt % | 0.01-5.17 |
| Viscosity at 98.9° C., cSt | 3.6-41.8 |
| Viscosity at 37.8° C. cSt | 14.2-1836.9 |
| ASTM D1160 distillation, °C. | |
| $T_{10}$ | 27-478 |
| $T_{50}$ | 385-504 |
| $T_{90}$ | 410-580 |
| Aniline point, °C. | 16.8-119.4 |
| Aromatic carbon content, % of total carbon | 1.2-51.6 |
| Hydrogen content, wt % | 9.61-14.58 |
| Molecular weight, by ASTM D2502 | 321-573 |

It should be noted that the aromatic carbon content was measured by the NMR technique and hydrogen content by the microanalyser. The microanalyser vaporites the liquid sample and converts the hydrogen content into water.

The hydrogen content can also be measured by the NMR technique. It was confirmed by Total Research Center that the NMR technique and the microanalyzer give essentially the same results for hydrogen content.

Fig. 2

Distribution of viscosity data is exponential

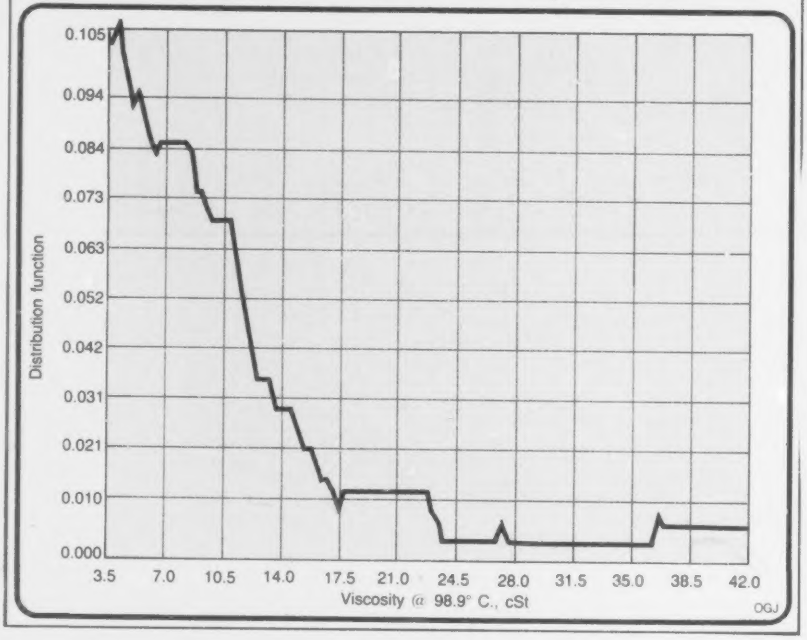
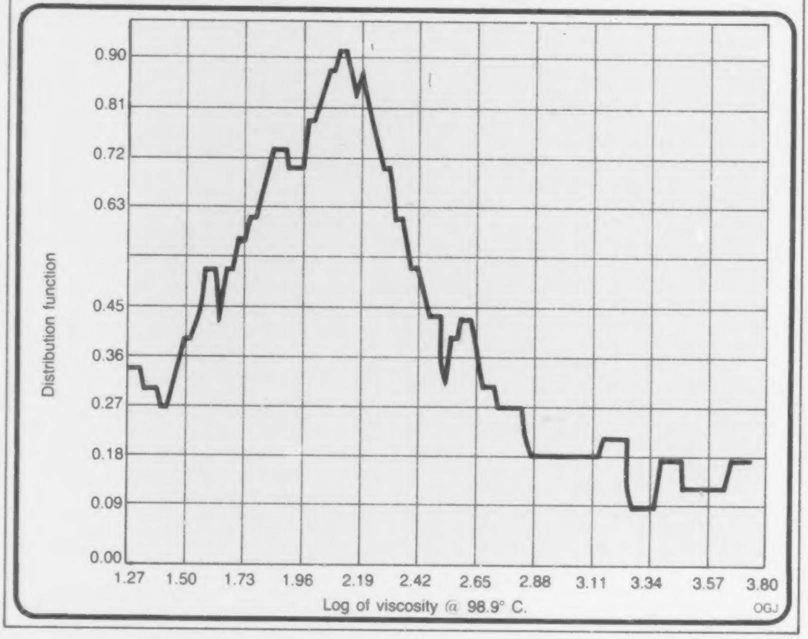


Fig. 3

Log of viscosity used in correlation



## New correlations

The new correlations were developed by multiple linear regression analysis using the data of 33 feedstocks. It is worth mentioning that the necessary condition for linear regression is that the statistical distribution of dependent as well as independent variables should be normal.

If it is not a normal distribution, the variable should be transformed in such a form so that it results in a normal distribution. Some of the possible transformations of variable x could be ln x, $e^x$, $x^2$, $\sqrt{x}$, etc.

Before carrying out the multiple regression analysis, each variable was statistically examined to verify the preceeding necessary condition. Fig. 1 shows the result of such an examination for the data of specific gravity which is a normal distribution.

When the data for viscosity at 98.9° C., (210° F.) were examined, it was a rather exponential distribution (Fig. 2).

Consequently, the normal distribu-

Table 1

## Comparison of Total correlations with other methods

| Correlation | Average absolute deviation | Average bias deviation | Maximum absolute deviaton |
|---|---|---|---|
| **Carbon content:** | | | |
| n-d-M | 5.14 | 4.67 | 12.99 |
| API | 2.88 | 2.53 | 9.13 |
| Total | 0.93 | 0.00 | 3.45 |
| **Hydrogen content:** | | | |
| Linden | 0.31 | −0.05 | 1.57 |
| Fein-Wilson-Sherman | 0.36 | 0.19 | 1.43 |
| Modified Winn | 0.19 | 0.07 | 0.86 |
| Total | 0.10 | 0.00 | 0.42 |
| **Molecular weight:** | | | |
| API | 62.0 | −62.0 | 180.9 |
| Maxwell | 63.3 | −63.6 | 175.0 |
| Kesler-Lee | 61.5 | −61.1 | 176.9 |
| Total | 10.6 | − 0.2 | 44.4 |
| **Refractive index:** | | | |
| API @ 20° C. | 0.0368 | −0.0367 | 0.0993 |
| Lindee-Whitter @ 20° C. | 0.0315 | −0.0131 | 0.0303 |
| Total @ 20° C. | 0.0021 | 0.0 | 0.0074 |
| Total @ 60° C. | 0.0021 | 0.0 | 0.0074 |

tion was obtained as shown in Fig. 3, by considering log of viscosity as a variable. Hence in the linear regression analysis, log of viscosity was used instead of viscosity as such.

After the statistical examination of all data, the following correlations were established as shown in Fig. 4-7:

- Aromatic carbon content—$C_A = -814.136 + 635.192\ RI_{20} - 129.266\ SG + 0.013\ MW - 0.340\ SUL - 6.872 \ln (VIS)$

- Hydrogen content—$H_2 = 52.825 - 14.260\ RI_{20} - 21.329\ SG - 0.0024\ MW - 0.052\ SUL + 0.757 \ln (VIS)$

- Molecular weight—$MW = 7.8312\ 10^{-3}\ SG^{-0.0976}\ T^{1.6971}\ AP^{0.1238}$

- Refractive index—$RI_{20} = 1 + 0.8447\ SG^{1.2056}\ (T + 273.16)^{-0.0557}\ MW^{-0.0044}$ and $RI_{60} = 1 + 0.8156\ SG^{1.2392}\ (T + 273.16)^{-0.0576}\ MW^{-0.0007}$

where:

$C_A$ = Distribution of aromatic carbon, % of total carbon

$H_2$ = Hydrogen content, wt %

MW = Molecular weight

$RI_{20}$ = Refractive index at 20° C.

$RI_{60}$ = Refractive index at 60° C.

SG = Specific gravity at 15° C.

SUL = Sulfur content, wt %

VIS = Viscosity at 98.9° C., cSt

T = Volumetric average boiling point of ASTM D1160 distillation, °C. = $(T_{10} + T_{30} + T_{50} + T_{70} + T_{90})/5$

AP = Aniline point, °C.

### Correlation comparison

The superiority of Total correlations was illustrated by comparing the measured and predicted values by the existing as well as Total correlations for the parameters in question.

**Aromatic carbon content.** The widely used n-d-M method[2] uses the value of the refractive index, density, molecular weight and sulphur content to predict $C_A$, $C_N$ and $C_P$ for olefin-free petroleum oils.

Other correlations are proposed by the API Data Book[3] which were originally developed by Riazi and Daubert [4 5] to predict the distribution of aromatic, naphthenic and paraffinic molecules. For the heavy fractions, they used the data of Van Nes and Van Western[6] to calculate the constants of their equations. It seems that the same data were also used by Van Nes and Van Western to develop the n-d-M method.

Hence, Riazi and Daubert's correlations for heavy fractions could be for structure distribution (like the n-d-M method) rather than molecule distribution. The predictibility of n-d-M, API and Total correlations are compared in Table 1 in terms of average absolute deviation, average bias deviation, and maximum absolute deviation. These three different types of deviations are defined as:

$$\text{Deviation} = x_{\text{predicted}} - x_{\text{measured}}$$

$$\text{Average absolute deviation} = \frac{1}{n} - \Sigma|\text{deviation}|$$

$$\text{Average bias deviation} = \frac{1}{n} \Sigma\ (\text{deviation})$$

where n is the number of data.

Fig. 4

Aromatic carbon content prediction

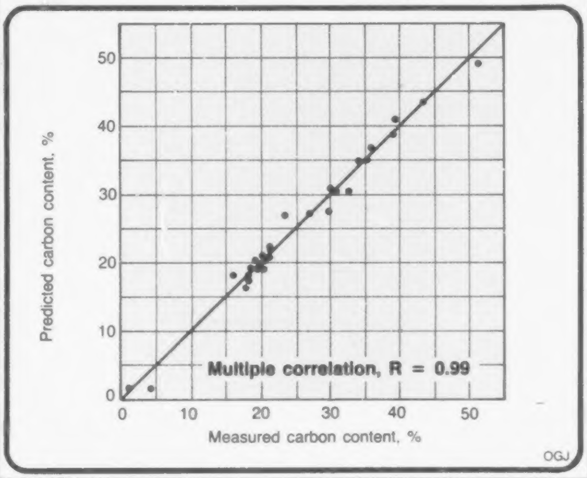


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Fig. 5

Hydrogen content prediction

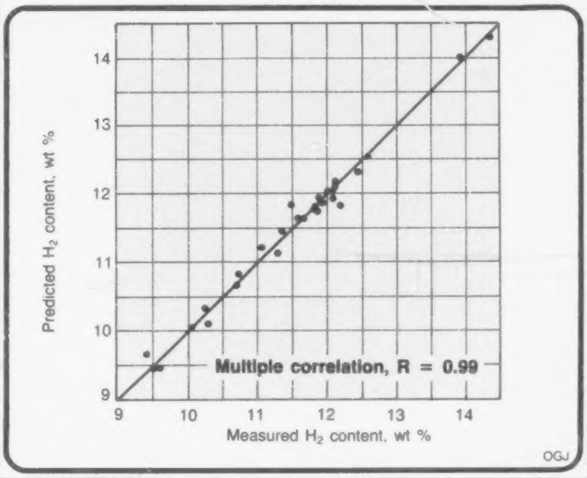

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Fig. 6

Molecular weight prediction

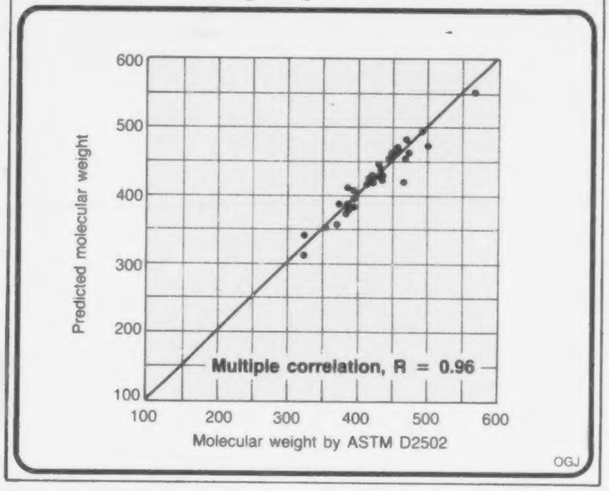

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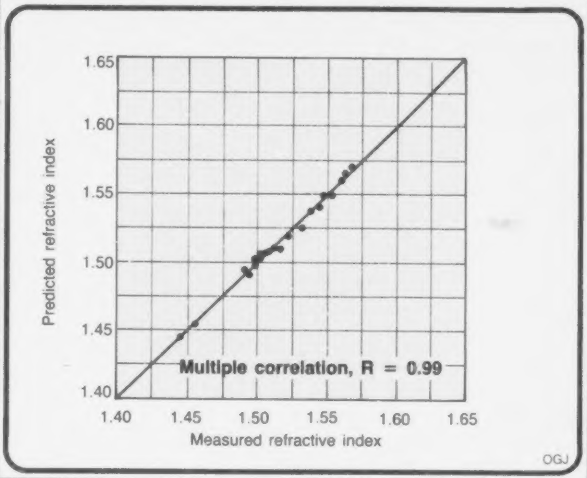
Fig. 7

Prediction of refractive index



OGJ

## The author ...

**Dhulesia**

Hasmukh Dhulesia joined the exploration and production department of Total Compagnie Française des Pétroles, Paris, in 1980 where he developed in-house computer programs for simulation of two-phase flow pipelines, simulation of pipeline transporting non-Newtonian oil, and prediction of hydrate forming conditions using the statistical thermodynamic theory.

Since 1982, he has been with the operational research department and is responsible for development of the software for monitoring, and day to day optimization of FCCU operations. Dhulesia earned a BSc (Hons.) degree in chemistry from MS University of Baroda, India, a BSc degree in chemical technology from Kanpur University, India, and MSc and PhD degrees in chemical engineering from the University of Manchester Institute of Science and Technology, England. He is the author of several papers on hydrodynamics and efficiencies of distillation trays and is a member of The American Institute of Chemical Engineers.

From Table 1, it can be seen that Total correlation predicts the aromatic carbon content more accurately than the n-d-M and API correlations. Since the API correlation predicts the carbon content more accurately than the n-d-M correlation, it supports the previous remark that API correlations for heavy fractions predict the carbon structure distribution rather than the molecule distribution.

**Hydrogen content.** In literature, there exists several correlations to predict the hydrogen content of hydrocarbon liquids.

The principal correlations are those of Linden[7], Flein-Wilson-Sherman[8], and Winn.[9]

The later correlation is in form of nomogram and was modified and expressed in form of equation for inhouse usage.[10]

Table 1 shows the comparison of these different correlations along with that of the Total correlation in terms of deviation from the measured value. This table indicates that the Total correlation is better than those existing as far as FCC feedstocks are concerned.

**Molecular weight.** The ASTM standard D2502 method[11] of calculating the molecular weight from the viscosity measurements, provides the best correlation. However, in the absence of viscosity measurements, the molecular weight can be estimated by API,[3] Maxwell,[12] or Kesler-Lee[13] correlations.

The predictibility of API, Maxwell, Kesler-Lee, and the Total correlations are compared in Table 1. It can be seen from this table that the Total correlation predicts the molecular weight close to that calculated by the ASTM D2502 method. It should be noted that the measured value of molecular weight in this table is the one calculated by the ASTM D2502 method.

**Refractive index.** If the measurement of the refractive index, which is used to predict $C_A$, $C_N$, $C_P$, and $H_2$, is not available, it can be estimated by API[3] or Landee-Whitter[14] correlations. Total correlations also predict the refractive index at 20° C. and 60° C. Table 1 shows the comparison of predictibility of all these correlations.

### Acknowledgment

The author thanks J. M. Bourdaire and J.C. Boudry (Total-CFP) for their suggestions and assistance for the statistical examinations carried out in this work, and Total Technique for providing the valuable analysis data of FCC feedstocks.

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# Refinery maintains optimum yields via resid HDS

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Resid hydroprocessing increases feedstock flexibility and refining profitability because gasoline conversion and liquid volume yields are sustained at optimum values.

The effects of feedstock impurities and composition on resid hydroprocessing (HDS) and its resultant impact on the performance of heavy-oil crackers have been evaluated from operations at Valero Refining Co., Corpus Christi, Tex.

The effects of catalyst selection on the optimum yields and plant profitability were also studied. And improvements in the technical aspects of the processes are currently being evaluated.

**Refinery configuration.** The Valero refinery is a residual oil upgrading plant designed to process 53,500 b/d of heavy Arabian resid. The design feedstock selection was based on availability and its poor quality.

The plant design provided Valero with sufficient flexibility to process a wide range of residual oils with high concentration of feed impurities, thus enhancing the optimization of the manufacturing profit margin.

Fig. 1 is a simplified block flow diagram of the Valero refinery. The principle units and their basic functions are:

- **Resid desalter**—The resid desalter is a three-stage, 53,000-b/d-capacity unit designed to remove inorganic chlorides to less than 1 lb/1,000 bbl. Efficient salt removal is essential because sodium chloride in the resid HDS feed contributes to both reactor bed plugging and process unit corrosion.

Reactor bed plugging is promoted because sodium sulfide deposits primarily on top of the catalyst bed, resulting in catalyst surface and interparticle fouling. Additionally, high percentages of sodium promote aromatic condensation and polymerization reactions, further increasing the mechanism of bed plugging.

This was confirmed in August 1984 when the guard reactor catalyst was replaced. Both the spent catalyst and top crust layer were analyzed for metal content. The sodium concentration was 50% higher in the crust layer when compared to its content in the catalyst.

The resid desalter also is used to remove 80-90% of the sediment (silt, sand, scale, tramp iron) contained in the resid, which is picked up during transportation.

- **Hydrogen reformer**—The hydrogen reformer, 50 MMscfd capacity, supplies the necessary hydrogen utilized for aromatic saturation and impurity removal in the resid HDS unit. Hydrogen product purity is maintained at 99.95 mole % by a pressure swing adsorption (PSA) hydrogen purification unit.

High hydrogen purity maximizes hydrogen partial pressure in the resid HDS unit reaction section, reducing catalyst cooling at high operating severities.

- **Resid HDS unit**—The resid HDS unit was licensed by Gulf and is one of the key process units necessary for the upgrading of atmospheric

Table 1

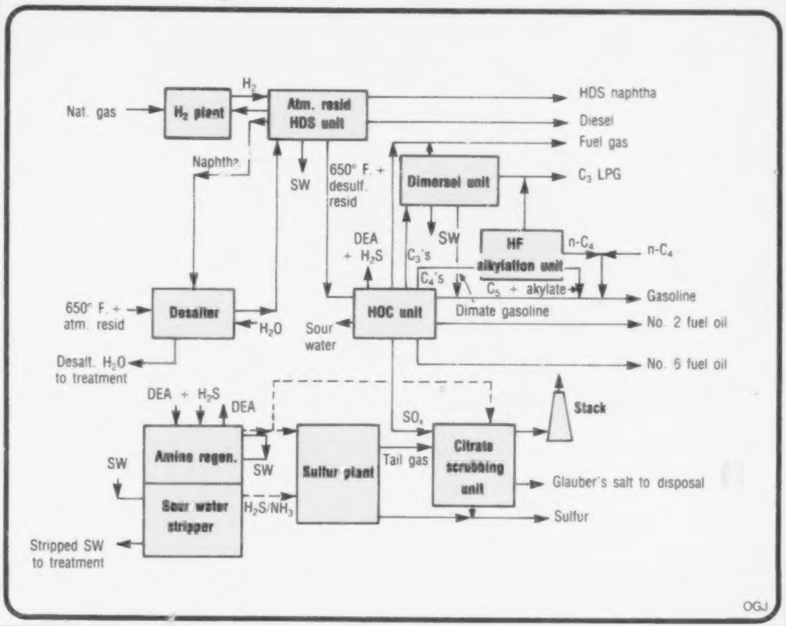
## Feed and product properties of heavy Arabian ATB

| Stream properties | Feed | Product, 650° F. |
|---|---|---|
| Gravity, °API | 12.6 | 20.15 |
| Sulfur, wt % | 4.34 | 0.5 |
| Nitrogen, wt % | 0.27 | 0.195 |
| Carbon residue, wt % | 13.3 | 5.9 |
| Metals content, ppm wt | | |
| Nickel | 30 | 7.8 |
| Vanadium | 95 | 11.5 |
| Viscosity, SFS at 122° F. | 500 | 250* |

*Estimated, based on unit performance

Fig. 1

## Refinery designed for resid feeds



tower bottoms (ATB) to a suitable catalytic cracker feed. It has a capacity of 46,100 b/d.

The resid HDS unit reduces feed impurities to acceptable levels and is operated at sufficient severities for conversion of polynuclear aromatics to mononuclear aromatics, naphthenes, and paraffins. Residual oil hydrogenation increases the crackability and selectivity of the feedstock as gasoline conversion is sustained between 60 and 65%.

- **Heavy oil cracker**—The heavy oil catalytic cracker (HOC) unit is the other key unit as hydrotreated resid is converted into marketable products such as unleaded gasoline and a No. 2 furnace oil blending component. Its capacity is 40,000 b/d. Light olefins are also produced (propylene and butylene) which are further upgraded to gasoline-blending components.

The HOC unit is also equipped with regenerator heat removal which is necessary for unit heat balancing when catalytically cracking atmospheric resids. The heat removal equipment produces high pressure steam which is used to produce electricity. In the heavy Arabian design case, power generation amounts to 51,000 kw.

- **Alky and Dimersol**—Both the 7,637-b/d HF Alkylation and 4,198-b/d Dimersol units contribute high octane blending components for unleaded-gasoline blending. The addition of the aforementioned units to the Valero processing scheme enables the refinery to meet recently imposed lead phasedown regulations (OGJ, Mar. 18, 1985, p. 92).

Other support units include a sour water stripper, amine treating unit, sulfur recovery unit, and an HOC flue gas $SO_2$ scrubbing unit (citrate unit).

### Resid HDS

The resid HDS unit is a feed preparation unit for heavy oil cracking. Failure to remove the impurities in the atmospheric resid results in a limited flexibility in feedstock selection and high yields of lower value products.

The principle reaction mechanisms are hydrodesulfurization and demetallation. Secondary reactions are denitrification, reduction of Concarbon through aromatic and asphaltene saturation, and hydrocracking.

To sustain the conversion at acceptable and economic levels (Table 1), the design operating pressure and catalyst volume are significantly higher when compared to conventional hydroprocessing units utilized for processing gas oil or for resid upgrading. A majority of the feed sulfur is contained in thiophenic molecules, which increases the difficulty of removal, because the size and complexity of the molecule inhibits effective sulfur adsorption onto active catalyst sites.

**Process variables.** The process variables that affect conversion or removal of sulfur and metals are as follows:

1. Reaction temperature. Reaction temperature is increased gradually above start-of-run conditions as catalyst activity declines. The mean average catalyst temperature range throughout the catalyst cycle life is 60° F.

As temperatures are increased above 750° F., adverse thermal reactions (aromatic condensation and thermal cracking), in addition to hydrocracking, are accelerated. Increased production of synthetic distillate, naphtha, and gas are witnessed at increasing temperatures in addition to higher levels of hydrogen consumption.

Higher reaction temperatures at constant catalyst activity promote an increase in the desulfurization and demetallation reaction rates. Generally, it is not desirable to raise catalyst weight average temperature (WAT) above design conversion rates because catalyst deactivation is accelerated from promoted thermal reactions.

2. Hydrogen partial pressure. The hydrogen partial pressure is a function of hydrogen purity, hydrogen recycle, hydrogen makeup rate, and reactor pressure. To minimize catalyst coking (deactivation) and to optimize the reaction rate, hydrogen partial pressure is sustained at maximum conditions.

Hydrogen makeup rate is dependent on reaction severity, feedstock composition, and the concentration of feedstock impurities. From operating experience, hydrogen consumption is distributed as follows:

- 120 scf/bbl for 1% sulfur removal
- 140 scf/bbl for 1% nitrogen removal
- 264 scf/bbl for conversion of polynuclear aromatics to mononuclear aromatics, naphthenes, and paraffins (based on heavy Arabian resid)

3. Liquid hourly space velocity.

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Based on a paper presented at the Akzo Chemie America Hydrotreating Symposium, Houston, May 24, 1985.

Fig. 2

## Flow diagram, Valero HDS unit

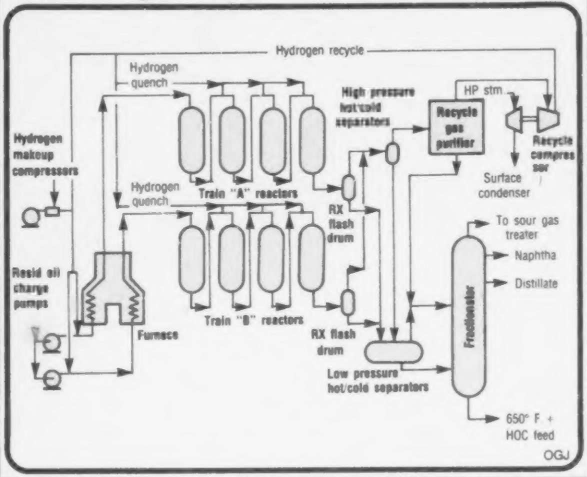
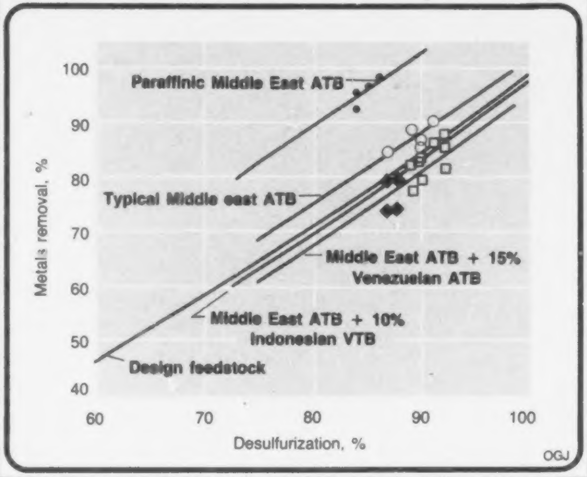


Fig. 3

## Feedstock varies considerably with type



The liquid hourly space velocity is a ratio of liquid flow per hour per volume of catalyst. The Valero unit has operated at liquid hourly space velocities 15% above design as economics favored increased throughput rates.

A 15% increase in space velocity requires an increase in reactor catalyst WAT of 5.5° F. to sustain hydrodesulfurization. This corresponds to a minimum reduction of catalyst cycle life equivalent to 30 days.

4. Feedstock. Since start-up in July 1983, Valero Refining has processed a myriad of atmospheric resids. Feedstocks have varied significantly in composition and impurities (Table 2).

As seen in Fig. 3, the reactivities of each feedstock have varied considerably with respect to type. The net conclusion from the accumulation of data is that feedstocks play an essential and key role in the performance of the resid HDS unit and the overall refinery yields.

Fig. 3 clearly shows a reactivity difference between the design feedstock and a paraffinic feed from the Middle East. The paraffinic material exhibited higher demetallation at lower desulfurization rates, permitting a reduction in catalyst reactor WAT. At lower operating severities, a reduction in cracking reactions, synthetic yields of diesel and naphtha, and hydrogen consumption is noted.

**Feed comparisons.** When comparing feedstock reactivities, one prominent factor is observed. Increasing feed viscosities reduces demetallation, indicating that feed viscosity has a significant effect on catalyst pore diffusion and liquid distribution through the catalyst reactor bed.

Other notable feedstock properties that affect the removal of sulfur and metals are asphaltenes, Conradson carbon, and feed molecular weight. In most cases, higher viscosity is a good indicator that the resid contains a higher percentage of asphaltenes (heptane insolubles), Concarbon, and organo-metallic compounds.

Feedstocks with lower reactivities and poor diffusivity characteristics adversely affect demetallation and desulfurization resulting in a significant increase in refinery operating cost, as HOC feed impurities are increased.

In Fig. 4, desulfurization and demetallation are plotted for the month of October 1984. During the month, three different feedstock blends were processed in the resid HDS unit at 53,500 b/d.

When a vacuum tower bottoms (VTB material was introduced in the feed blend, an immediate drop in demetallation to 82 wt % is noted. Removal of the VTB stream restores the demetallation to 88%.

A second test was implemented at the end of the month when a Venezuelan atmospheric tower bottoms (ATB feedstock was introduced at 15% of the feed blend. Both a decrease in desulfurization rate to 88% and demetallation to 75% are noted.

During the month, the catalyst WAT, hydrogen partial pressure, and liquid hourly space velocity were maintained constant. A 10° F. increase in catalyst WAT was implemented during the Venezuelan feed test run, but had little or no effect on the demetallation reaction rate.

This clearly substantiates early research that feedstock has a dramatic effect on demetallation, as the reaction mechanism is primarily dependent of pore diffusion.[1] In comparing light Arabian ATB to a Venezuelan ATB, the molecular weight and asphaltene concentration differ by a factor of nearly two. (Average molecular weight of light Arabian is 490 lb/lb-mole). The larger molecule, which exhibits higher viscosities and impurity concentration, limits pore diffusion and thus demetallation, adversely impacting refinery yields and plant profitability.

Organo-metallic compounds, sulfur, nitrogen, Concarbon, and carbon-to-hydrogen ratio all have a significant impact on HOC yields.

**Organo-metallics.** Metals such as vanadium and nickel are present in high concentrations in the resid HDS feed. A 1% reduction in demetallation on a heavy Arabian resid results in a vanadium increase in HOC feed equivalent to 0.95 ppm, which is equivalent to 0.0674/bbl or $1.32 million/year in HOC catalyst replacement costs.

Increasing the vanadium level to 4,000 ppm from 3,500 ppm on the HOC catalyst will reduce the catalyst replacement costs to $0.059/bbl or $1.15 million/year. The HOC catalyst addition is based on the vanadium concentration in the feed. Since the nickel does not adversely affect the activity of the catalyst because the dehydrogenation reaction mechanism is neutralized through the addition of antimony.

The vanadium, however, reacts or fluxes with the zeolite resulting in permanent deactivation, and a significant reduction in the equilibrium activity as represented in Fig. 5. Increasing the vanadium level from 3,000 ppm to 3,500 ppm on catalyst results in a microactivity loss equivalent to 3%.

The lower microactivity leads to a reduction in gasoline selectivity and gasoline conversion (Fig. 6), from a typical yield of 66% down to 63%.

Table 2

## Properties of feedstocks and products

| Feedstock<br>Stream properties | Paraffinic Mid-East ATB<br>Feed | Product* | Typical Mid-East ATB<br>Feed | Product* | Mid-East ATB + 15% Venezuelan ATB<br>Feed | Product* | Mid-East ATB + 10% Indonesian VTB<br>Feed | Product* |
|---|---|---|---|---|---|---|---|---|
| Gravity, °API | 20.0-21.0 | 24.5-25.0 | 17.2-17.5 | 23.0-23.6 | 16.3-17.0 | 21.0-22.1 | 15.5-17.5 | 22.0-23.5 |
| Metals (V + Ni), ppm | 13-16 | 0.4-1.5 | 22-26 | 1.0-3.5 | 85-94 | 12.4-19.7 | 60-70 | 7.0-16.5 |
| Sulfur, wt % | 1.8-1.9 | 0.22-0.30 | 2.7-3.0 | 0.25-0.35 | 3.0-3.1 | 0.37-0.38 | 3.1-3.6 | 0.27-0.37 |
| Viscosity, SFS at 122° F. | 39-41 | 30-33 | 61-68 | 34.5-36.9 | 71-91 | 40.0-52.1 | 75-110 | 40.0-52.5 |
| Concarbon, wt % | 3.9-4.2 | 1.1-2.0 | 6.0-7.7 | 1.8-2.5 | 7.3-8.4 | 3.5-4.0 | 9.0-10.5 | 2.5-4.4 |
| Nitrogen, ppm | 1600-2000 | 818-1164 | 1700-1900 | 947-1136 | 2400-2550 | 1465-1590 | 2950-3450 | 1300-1916 |
| Asphaltene, wt % | 0.3-0.7 | 0.1-0.35 | 1.1-1.5 | 0.14-1.1 | 1.9-2.2 | 0.17-0.65 | 2.1-3.5 | 0.61-1.39 |

*650° F.

The apparent conversion is reduced to 78.2% from 81.2%.

The net economic loss from operating at higher metals level on catalyst (3,500 ppm) is 0.35/bbl or $6.83 million/year. Catalyst savings at higher metals loading on catalyst is $0.130/bbl or $2.54 million/year (Fig. 7).

This is based on 11 ppm vanadium in the HOC feed. Depending on the economic climate, the aforementioned economic conditions could change, but at current gasoline prices it is more desirable to optimize gasoline conversion. An increase in 1% demetallation rate in the HDS unit would increase HDS catalyst cost (from deactivation) $0.0047/bbl or $92,000/year.

In review of the organo-metallic impurities, removal of metals in the resid HDS unit is most desirable.

**Aromatics and Concarbon.** Most of the residual oil feeds purchased by Valero contain a high percentage of condensed carbon rings reducing the hydrogen-to-carbon ratio and API gravity. A majority of these asphaltic molecules are termed coke precursors because a high percentage of the polynuclear aromatics yield coke and gas within the reaction section of the catalytic cracker, resulting in lower gasoline yields.

The resid HDS unit, through hydrogenation, converts the polynuclear aromatics to mononuclear aromatics, naphthenes, and paraffins. From operating experience, a Concarbon reduction of 60% is achieved on most feedstocks.

A typical increase in API gravity is 8°, indicating the significant addition of hydrogen and/or aromatic saturation. Feedstocks that are higher in asphaltene concentrations are still deficient in hydrogen in the hydrotreated product.

This was observed when processing a feed blend containing 15% of a Venezuelan ATB. Upon introduction of the Venezuelan material, HOC gasoline yields dropped an average of 3.0% (Table 3).

Metals levels on HOC catalyst were maintained constant during the test.

Fig. 4

## Feedstock has dramatic effect on demetallation

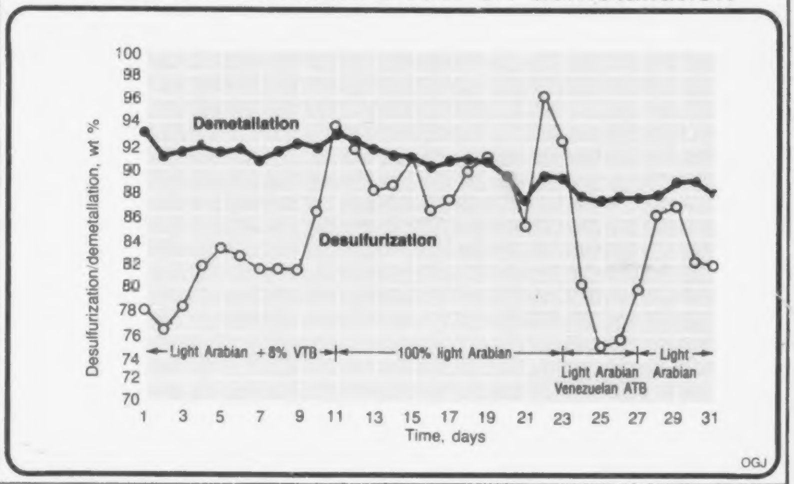


Fig. 8 shows the difference in gasoline yields based on API gravity of the feed. A drop in gasoline yields is significant at lower API gravities, indicating a hydrogen deficiency of the hydrotreated HOC feed and a net reduction in crackability.

**Nitrogen effects.** The more asphaltic the oil, the higher the nitrogen content, which correlates well with the percent Concarbon in the feed. However, nitrogen removal in the resid HDS unit is significantly less when compared to Concarbon reduction.

Typical denitrification rates average 40 wt %, approximately 5% above design. This indicates that a majority of the nitrogen compounds are bound to the stable complex asphaltene molecules that undergo little or no compositional change in the resid HDS unit. The basic nitrogen in the HOC feed inhibits catalytic activity in the riser because active acid sites are temporarily neutralized.

A contribution to gasoline yield loss when switching to the Venzuelan feed blend is evident as nitrogen levels in the hydrotreated product increased from 1,150 to 1,550 ppm. The total gasoline loss for the Venzuelan feed blend was 3.0%.

Although the yield variation was attributed mostly to the change in the API gravity (aromaticity of the feed blend), a recent pilot plant test suggests that basic nitrogen has the strongest effect on catalyst activity and gasoline yield. Both API gravity and Concarbon exhibit the strongest effect on selectivity. From a review of several feedstocks, it was derived that 62% of the gasoline yield variation was attributed to basic nitrogen in the feed.[2]

Analyzing the yield decline, upon the introduction of the Venezuelan resid, a 1.86% gasoline loss is the result of increased levels of basic nitrogen. This corresponds to a $4.278 million loss/year at a total nitrogen weight percent rise of 400 ppm wt. Improvement in nitrogen removal in the resid is important in order to sustain optimum gasoline yields.

### Catalyst effects

From operating experience, and several pilot plant studies,[13] the two most important factors that affect the rate of demetallation is feedstock and catalyst pore size. Since Valero Refining Co.'s primary objective is to maximize feedstock flexibility, resid HDS

Table 3

## High asphaltene content feeds reduce HOC gasoline yields*

| Yields, vol % | Design heavy Arabian | Light Arabian | Light Arabian plus 15% Venezuelan crude |
|---|---|---|---|
| Propane-propylene | 9.9 | 9.52 | 9.12 |
| Butane-butylene | 16.8 | 13.95 | 12.77 |
| Gasoline | 55.7 | 65.31 | 62.33 |
| Light cycle oil | 15.1 | 14.52 | 17.43 |
| Slurry | 7.4 | 4.01 | 4.4 |
| Vol gain | 4.9 | 7.31 | 6.05 |
| Coke, wt | 11.8 | 8.73 | 8.84 |
| Gas, wt % | 3.4 | 3.4 | 3.78 |
| Gasoline, RON/MON | | 90/80.1 | 90.3/80.2 |

*Typical data at a vanadium level on catalyst equivalent to 3,400 ppm and reactor temperature of 970° F.

catalyst selection plays a key economical role in optimizing refinery yields.

**Pore diameter.** Increasing catalyst pore diameter permits a rise in feedstock viscosity as both effective diffusivity and demetallation are improved.[3] Since demetallation is autocatalytic,[4] the reaction rate should theoretically increase throughout the catalyst cycle provided pore mouth plugging by coke and metal sulfides is minimized.

Additionally, researchers[1 3 4] confirm that the demetallation reaction mechanism is first order with respect to pore diameter. In reviewing the feedstocks processed to date, heavier molecular weight resids exhibit poor demetallation characteristics.

Raising reaction temperatures increased demetallation because asphaltene de-polymerization is promoted allowing fragmented diffusion. Bulk fluid viscosity is also reduced, improving flow distribution through the catalytic bed. However, adverse coking/cracking reactions are increased, resulting in higher coke deposition and increasing catalyst deactivation rates.

**Catalyst loading.** As pore diameter is increased, catalyst surface area is decreased, resulting in lower catalytic activity for hydrodesulfurization and denitrification. Therefore, a balanced blend of catalyst, optimizing both porosity and activity, is necessary. This led Valero to request several pilot plant studies from the licensor (Gulf Research & Development) for determining the optimum catalyst loading schemes.

The existing loading scheme consists of three catalysts. The first reactor is loaded with 11 wt % of a demetallation catalyst. Then 89 wt % of two different grades of hydrodesulfurization/hydrodemetallation catalyst are loaded. The two grades are similar in pore size and surface area, but they vary significantly in chemical composition.

Gulf Research & Development worked closely with Akzo Chemie America on the development of an improved demetallation catalyst. This catalyst was first commercially tried in the Valero refinery HDS unit.

The major change is the optimization of pore structure as Gulf Research & Development confirmed that demetallation was directly related to the size of the macropore. Activity for desulfurization was related to catalytic metals contained in the micropore structure.[6]

The primary objective of the pilot plant studies was to determine optimum demetallation catalyst loading for increased demetallation, lower HOC catalyst costs, and a higher metals retention capacity for maximizing catalyst cycle life. The tests utilized similar feed blends that have been processed at the refinery.

The results of the test indicated that demetallation could be increased by increasing demetallation catalyst but at the expense of activity and desulfurization. Reactor catalyst WAT can be raised to maintain desulfurization at desired levels but a significant reduction in catalyst life would be experienced.

**Aging and deactivation.** Catalyst deactivation in resid hydroprocessing, can be broken down into three distinct parts. Rapid deactivation was noted early from the equilibrium laydown of carbon promoted by high catalytic activity and the deposition of metal sulfides on the catalyst surface.

Metal sulfides (nickel sulfide, NiS and vanadium sulfide, $V_3S_4$) have catalytic activity for hydrogenolysis but are lower in activity when compared to the catalyst metals impregnated on the fresh catalyst.

The final deactivation segment is denoted by rapid activity loss brought about by catalyst pore mouth plugging. In between, "catalyst deactivation is slow and is directly related to the concentration of organo-metallics in the feed and not the concentration

Fig. 5

Vanadium reduces equilibrium activity

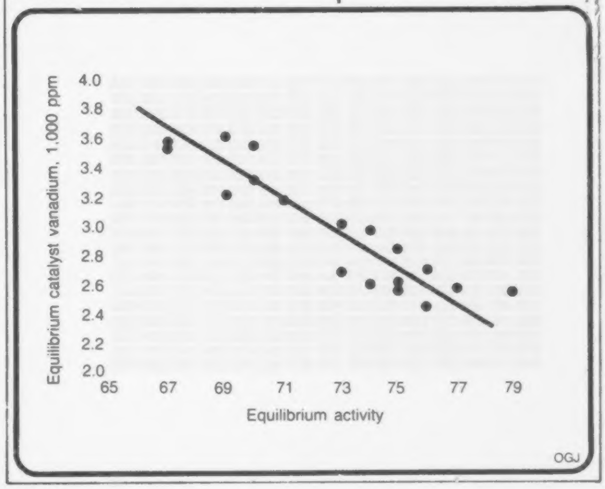


Fig. 6

Gasoline drops at high vanadium

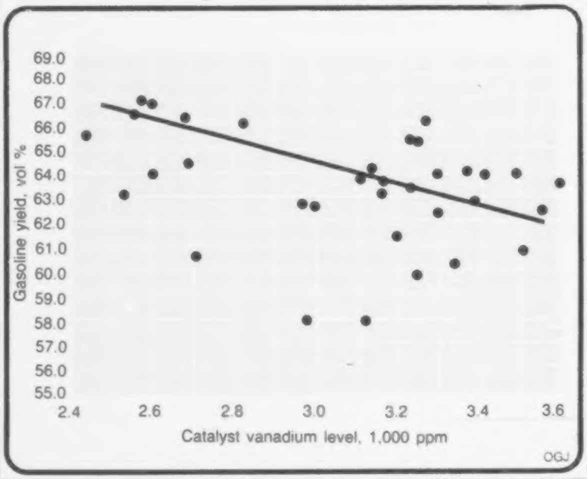


Fig. 7

Catalyst costs decrease at higher metals loading

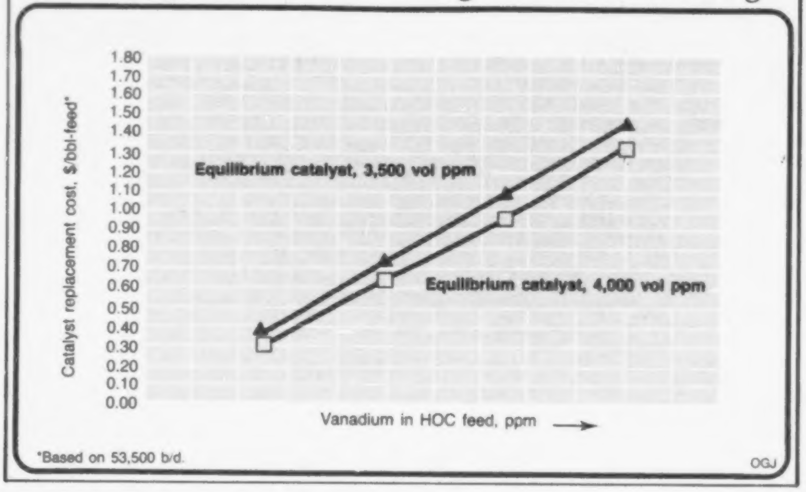


Fig. 8

Vanadium and API gravity effects on gasoline yields

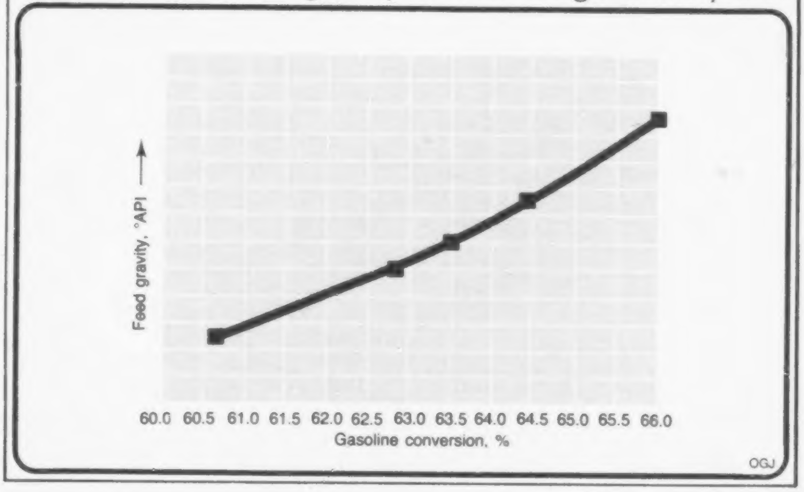
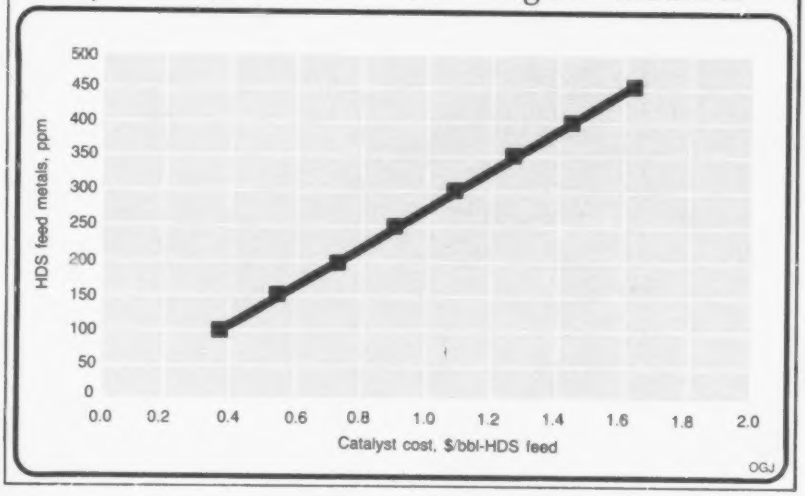


Fig. 9

Catalyst deactivation and feed organo-metallics



of coke precursors."[5]

Early in the catalyst cycle life, the aforementioned statement was verified as depicted in the Valero unit deactivation curve (Fig. 9). The deactivation rate correlated well with metals loading on catalyst.

However, most recently, as severity was increased to sustain conversion rates on higher viscosity feedstocks, a noted rise in deactivation from a mechanism other than metal sulfide deposition is noted. The increase in deactivation is no doubt due to an increase in carbon deposition promoted by a combination of higher severities and increasing concentration of coke precursors.

Nevertheless, the catalyst life of the Valero unit has exceeded expectation in terms of barrels per cubic foot processed. This is primarily the result of processing feedstock that is less severe in terms of impurities (organometallics).

Another mechanism of catalyst life decline is interparticle plugging resulting in higher reactor bed pressure drops. Interparticle plugging has resulted in the change-out of the catalyst in the first reactor in August 1984. From analysis of the crust layer, high sodium and iron contents were observed. Past experience in other units[5] verifies that iron sulfide buildup on the catalyst surface is much faster, when compared to pore-mouth plugging of vanadium and nickel sulfides.

## Improvement evaluations

Although Valero Refining Co. has a wide range of feedstock processing flexibility with the addition of resid hydrotreatment, high levels of organometallics, basic nitrogen, and Conradson carbon in certain feedstocks increase plant operating costs significantly. Additional economic improvements in the low-quality feed-handling processes are under evaluation.

**Tin addition.** Reducing the effect of organo-metallics on both resid hydroprocessing catalyst life and costs, along with its effect on HOC catalyst deactivation, is currently in review. As noted in Fig. 10, HDS catalyst cycle life is shortened dramatically as metals are increased from 100 to 200 ppm metals in the feed.

Additionally, higher organo-metallics in the HDS feed result in a higher feed metal concentration in the HOC feed. Metals contribute to additional HOC catalyst costs and/or profit losses from operating at lower gasoline conversions.

A recent development is the addition of tin to HOC feed. The tin reacts with vanadium to form a vanadium-tin complex, inhibiting the production of vanadium pentoxide, reducing va-

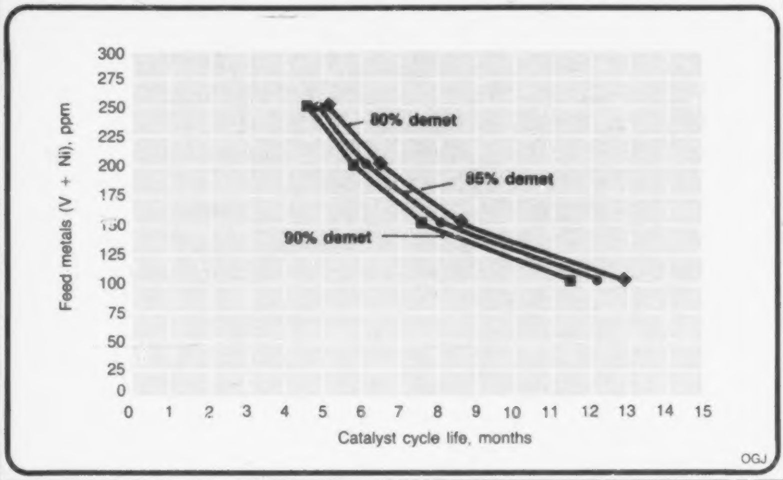


Fig. 10

HDS cycle life shortened by organo-metallics

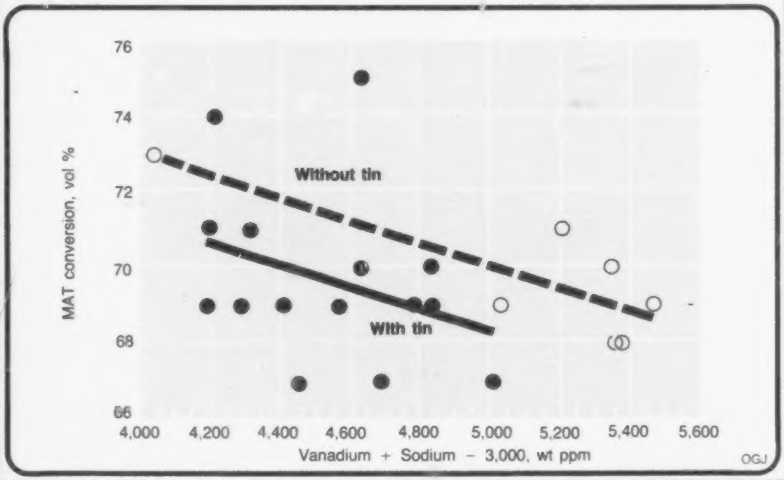


Fig. 11

Adding tin to feed increases MAT

nadium mobility and zeolite deactivation.

The net result is a 1.5-2.0% gain in microactivity at a constant level of vanadium on catalyst. Tin addition was implemented in March 1985. Initial observations indicate a savings of $3,000/day in HOC catalyst cost (based on 11 ppm vanadium in the feed, Fig. 11).

**Catalyst upgrading.** Other developments are in HOC catalyst upgrading for tolerating higher vanadium loadings. The use of a vanadium sink catalyst will be implemented in June 1985. Pilot plant testing indicates a 2.3% increase in conversion at the same vanadium level on catalyst.

Optimization of the demetallation reaction, and catalyst cycle life, can be implemented though the upgrading of the resid HDS catalyst pore size, activity, and loading configuration. Selection of a single feedstock would allow the optimization of the catalyst loading scheme and maximize refinery yields and the margin of profitability.

Increasing the weight percent of nickel on catalyst will improve denitrification but at the expense of desulfurization. Hydrogen consumption and Concarbon reduction would also increase at higher nickel levels on catalyst.

Altering the catalyst support material to improve coke stability and catalyst life is also being implemented by several catalyst manufacturers. Increased coke stability will permit a higher temperature operation without accelerating the catalyst deactivation rate.

Continued catalytic development work both in resid HDS and HOC catalyst will reduce operating costs and increase feedstock flexibility for the Valero refinery.

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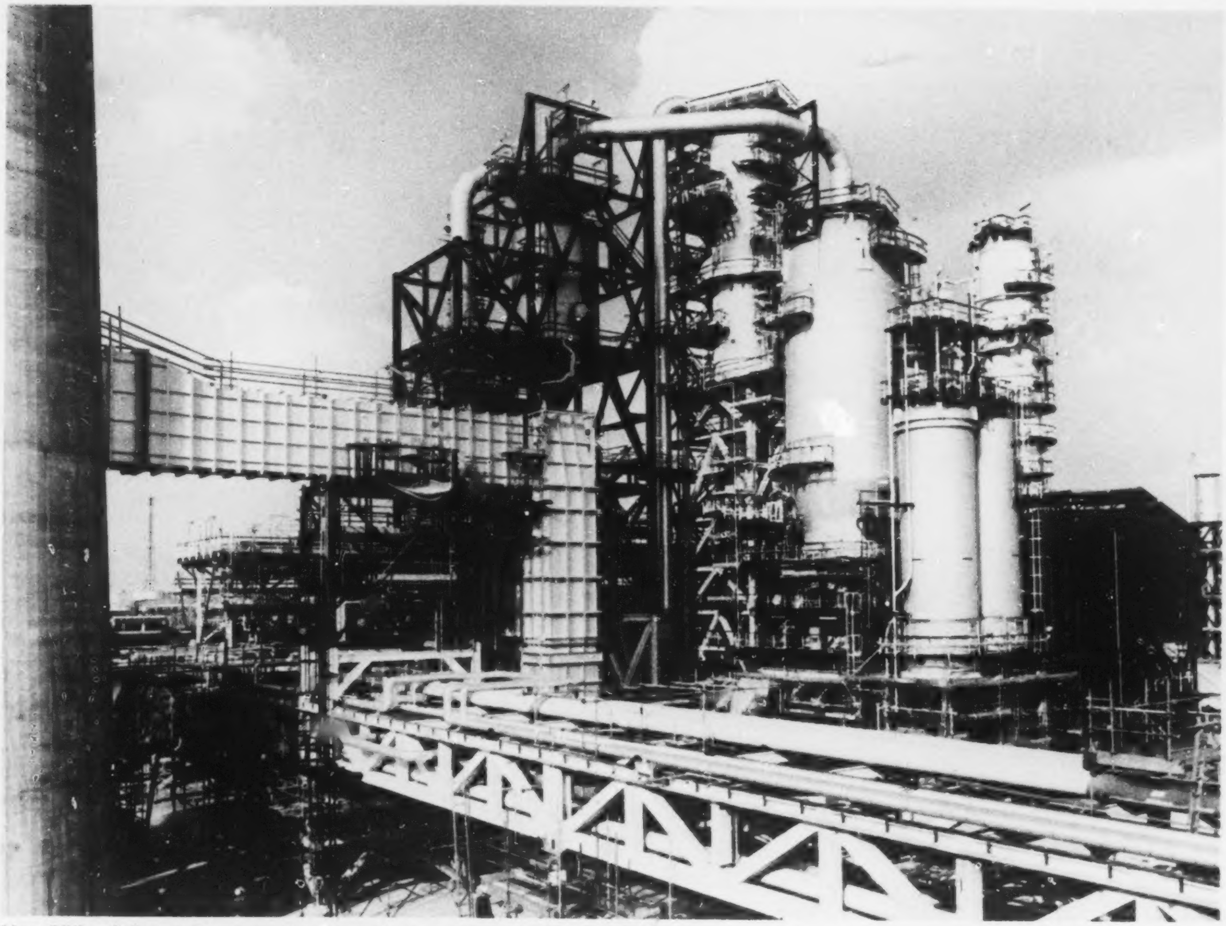

**New FCC unit** boosts Humber refinery's ability to produce high value products.

# FCC unit on line at Conoco's Humber refinery

Conoco U.K. Ltd. has placed a 35,000 b/d fluidized catalytic cracker on stream at its 130,000 b/d Humber refinery on the east coast of England.

Modular techniques adapted from offshore construction enabled Conoco to set a world record for taking a plant of this type and complexity from the drawing board to full operation in just 2 years, said Duane Skogen, Conoco managing director for refining.

The £60 million ($88.2 million) cracker, designed by Badger BV of Holland, employs process modules preassembled by Fabricom, Ghent, Belgium. Structural steelwork was by Humberside Fabrication Services and Techmac, both British companies.

The FCC, designed to increase the plant's flexibility to produce high value products such as low lead and unleaded gasoline, is the biggest single investment made at the refinery since it opened in 1970.

Other spending during the past 3 years has amounted to £100 million ($147 million) for units such as a catalytic polymerization plant to increase production capacity for high octane gasoline.

The Humber refinery is the only plant in Britain producing petroleum coke. Flexibility of the unit has given Conoco an edge in the gasoline market, where it operates under the Jet and Global brands.

Among other downstream projects in Britain, Conoco has a joint venture under way with Calor Gas Co. to build two LPG storage tanks in chalk caverns 600 ft underground near the Immingham refinery.

A 60,000 metric ton propane cavern was opened last September, and a similar sized butane cavern will be completed in June. ▪

# Studies reveal shot-coke microstructure, suggest ways to minimize its formation

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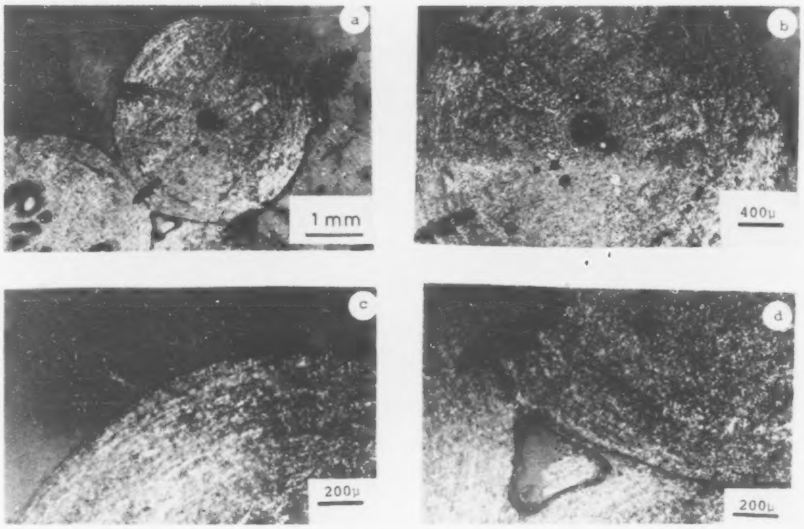


**Shot coke** is composed of a very dense structure with a limited number of pores and fissures as shown in these microphotographs (Fig. 1).

Table 1

## Analyses of residues

| Sample | Carbon | $H_2$ | $N_2$ | Sulfur | Saturates | Aromatics | Resin | Asphaltenes, wt % |
|---|---|---|---|---|---|---|---|---|
| Minas VR | 85.9 | 12.1 | | 0.2 | 43.2 | 18.9 | 35.8 | 3.1 |
| Maya VR | 83.0 | 9.2 | 0.9 | 5.7 | 7.5 | 24.2 | 25.8 | 42.5 |
| Kafji VR | 86.3 | 7.6 | | 4.4 | 0 | 33 | 45 | 22 |
| FCC DO | 89.6 | 9.4 | | 0.7 | 24 | 71 | 5 | 0 |

The microstructure of shot coke has been revealed by experimental studies of the formation of various petroleum cokes by carbonization of heavy resids. The results of these experimental studies indicate the mechanisms responsible for the formation of shot coke, and they suggest procedures to minimize the formation of shot coke in commercial delayed cokers.

The structure of shot coke is described by the use of montage microphotographs, comparing the structure to that of sponge coke. The photographs reveal the fine-mosaic, high-density structure of shot coke.

Previous studies indicate that shot coke appears to be encountered more frequently when processing heavy resids. Marsh, et al.,[1] and Derbyshire, et al.,[3] observed the fine-mosaic texture of shot coke and discussed the mechanism of its formation.

Additional information regarding the formation of shot coke is described in NPRA Q&A transcripts.[5] Lieberman[6] suggests the growth of shot coke and its settling in the liquid phase. This study provides additional information to help decrease the formation of shot coke.

**Experimental procedure.** Shot cokes and petroleum residues were provided by major U.S. petroleum companies. Table 1 summarizes the analytical data on these cokes and residues.

The structure of the cokes was examined by the use of an optical microscope after conventional polishing of the coke samples. The montage photographs were taken using a point-counting stage.

Carbonization of the petroleum residues was performed in a tube bomb heated in a molten tin bath or in heated, fluidized sand.[7] Prior to carbonization, the residues were preheated under variable conditions to simulate the preheating that takes place in the heater tubes of a commercial delayed coker. The carbonization pressure was varied while the carbonization temperature was held constant at 500° C.

**Coke structure.** Fig. 1 is a montage of several microphotographs of shot coke. Shot coke was seen to be individual 1 mm to 100 mm diameter spheres, and a cluster of spheres resembling a bunch of grapes adhering to each other at their contact surfaces.

Individual spheres of shot coke had similar structural characteristics. They were quite spherical and very dense with limited numbers of pores and fissures (Fig. 1). The optical texture of the shot coke was principally fine mosaic, much finer than that of sponge coke (Fig. 2).

Some details of the distribution of the textures are seen in the montage. The fine mosaic units at the center of the sphere are oriented in a completely random arrangement (Fig. 1b), whereas the mosaic units are oriented concentrically around the periphery of the sample (Fig. 1c).

Some spheres have larger units of mosaic texture around the pores (Fig. 1b). The contact surfaces of the spheres exhibit larger mosaic units which tend to be arranged in one direction, probably reflecting the concentric arrangement in the peripheries of the spheres (Fig. 1d).

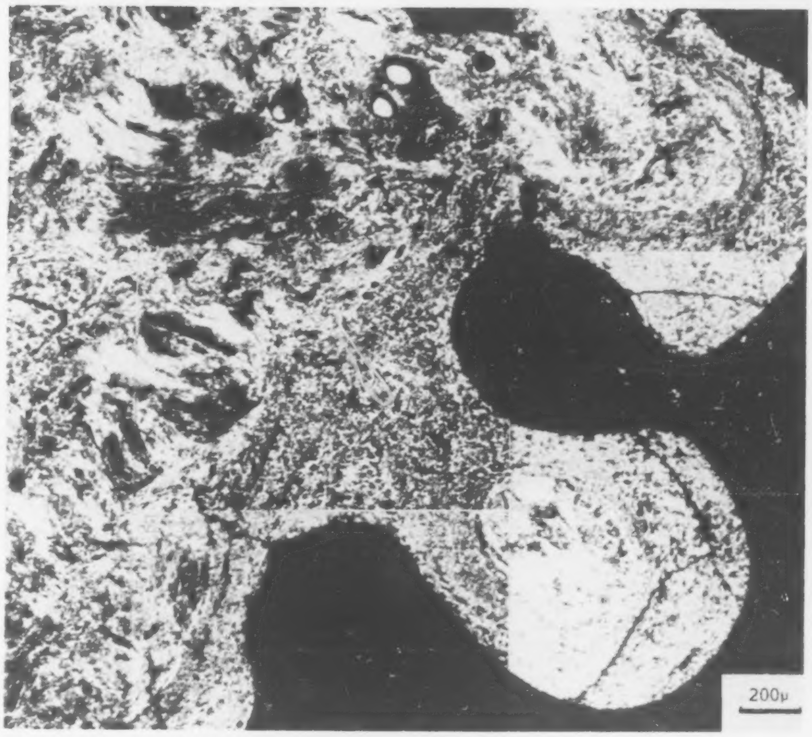
In contrast, sponge coke contains a mixture of optical textures: domain, flow, coarse mosaic, and fine mosaic (Fig. 2). There are many pores and fissures at the boundries of different textures, as often observed in sponge coke.[8, 9]

Some of the fine mosaic textures form islands or peninsulas of high-density which are connected to the parts of the typical sponge-coke structure (Fig. 2). Such parts appear to be relatives of the shot cokes, although

Table 2

## A sequence of steps for shot coke formation

1. Thermal cracking and condensation of residue into light paraffins, long paraffins, medium aromatics, heavy aromatics, and oxidized polar fraction.
2. Severe devolatilization of light paraffins and medium aromatics (solvent-fraction) for more cracked oil, leaving long paraffins, heavy aromatics, and oxidized polar fraction.
3. Phase separation of low mutual solubility causing spherical nucleation of heavy aromatics and polar fractions in the paraffin matrix, and random mosaic at the center of the sphere because of very high viscosity.
4. Sphere growth during turbulence caused by rapid gas flow, collecting heavy and less heavy aromatics, leading to the spherical orientation. Less heavy aromatics give larger texture at the pheriphery of the sphere.
5. Larger coke caused by rapid turbulence since the sphere moves, collecting aromatic molecules until they become large enough to precipitate to the bottom, or on the wall of the drum.
6. High viscosity prohibits complete coalescence of precipitated spheres when adhered, although a larger mosaic is developed at junctions because of collected aromatics.
7. Little devolatilization of light aromatics from the sphere leaves few pores, around which a larger mosaic texture develops.
8. Complete devolatilization of the matrix through pyrolysis and stripping, leaving shot cokes alone.



**Sponge coke** has many pores and fissures as seen in this micrograph (Fig. 2).

they are not complete spheres.

**Coke from Minas resid.** Fig. 3 shows a series of cokes obtained from Minas vacuum residue under variable conditions. A single-stage carbonization at 500° C. under 1, 4, and 26 atm pressure produced flaky coke of coarse mosaic structure with many pores (Fig. 3a), a lump coke of coarse and flow texture with less pores (Fig. 3b), and a lump coke of essentially flow texture uniaxially oriented (Fig. 3c).

In the last coke, flow textures and pores were oriented parallel to the axis of the tube bomb. Such a coke can be called needle coke, similar to that produced in commercial cokers.[10]

Some fine-mosaic areas were observed, especially in the coke produced under 1 atm pressure. However, the fine mosaics were scattered in the areas of larger optical textures, and contained many pores and voids as does sponge coke.

A two-stage carbonization at 500° C., under variable pressures, emphasized the separation of fine mosaic areas from those of larger mosaic and flow texture (Figs. 3d and 3e). Some fissures are clearly observable at the borders of the textures, tending to isolate the areas of fine mosaic texture.

Pores in the areas appeared to decrease by the two-stage carbonization. Although 1 atm pressure at the second stage provided some pores, even after carbonization at 6 atm in the first stage, a pressure of 6 atm in both stages appeared to give semispherical areas of fine mosaic texture without pores. This is common to the structure of shot coke, although the complete spherical shape was not produced.

**Cokes from Maya resid.** Maya residue provided a fine moasic structure in all areas regardless of the conditions (Fig. 4). A pressure of 4 atm failed to increase the size of the optical texture.

The carbonization conditions, however, influenced the density of the coke. Carbonization less than 1 atm produced a lump coke with many pores with very thin walls (Fig. 4a). A higher carbonization pressure of 4 atm increased the density of the lump coke, decreasing the pores and thickening the walls (Fig. 4b).

The two-stage carbonization further decreased the pores in the resultant coke, especially when the pressure of the second stage was high (Figs. 4c and d).

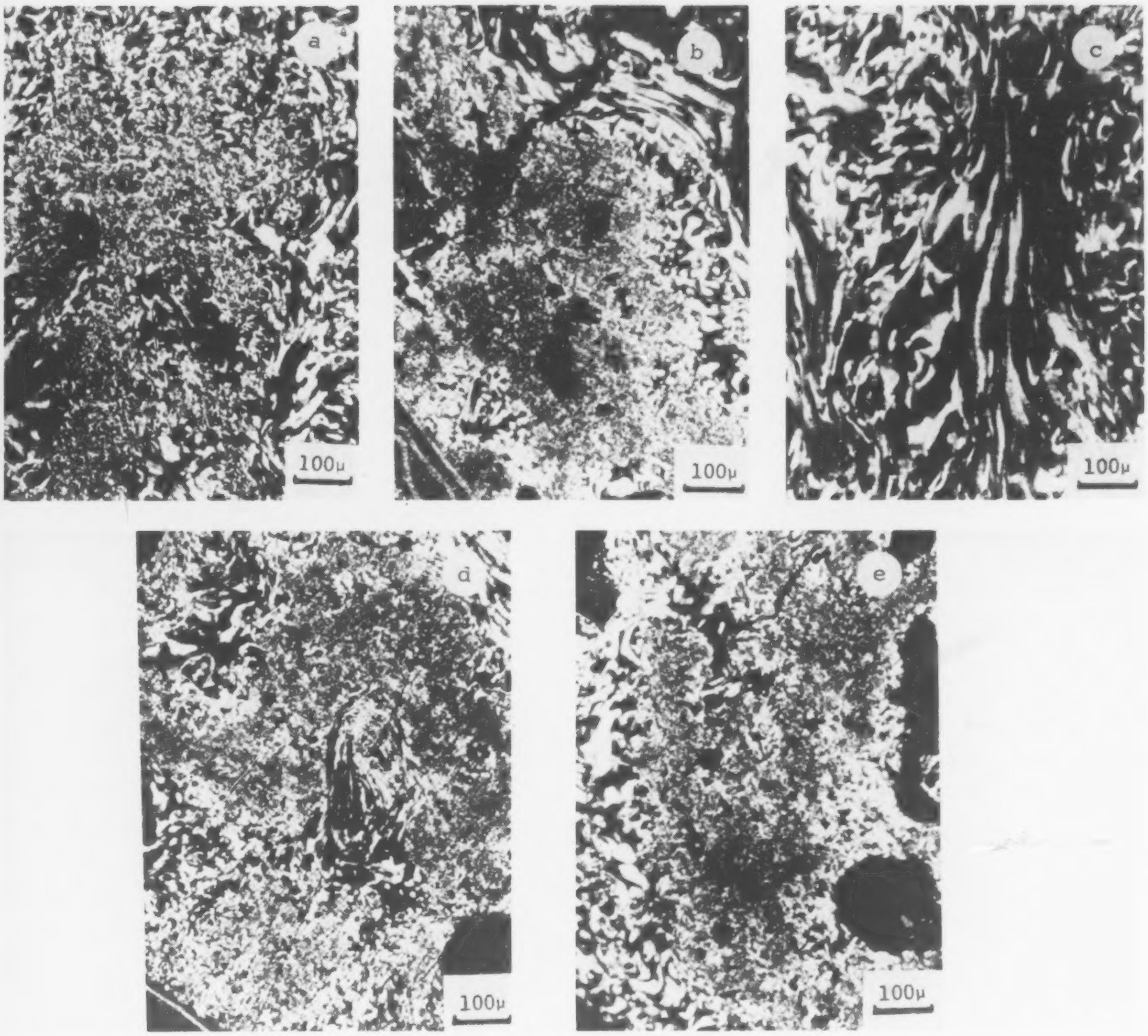
**Carbonization of blends.** Fig. 5 shows microphotographs of cokes produced from residue blends. Since all blends provided lump cokes under the test conditions, their top and bottom parts were separately observed.

Some cokes exhibited very different features according to the location. The cocarbonization of Maya vacuum resid and Minas vacuum resid provided very different features in the top and bottom parts of the coke. A very large deformed mosaic texture with some macropores is observed at the top, whereas a very fine mosaic texture is concentrated at the bottom, forming isolated areas with less pores (Fig. 5a).

The blending of Maya vacuum resid with fluid catalytic cracker (FCC) decant oil and Kafji residue gave cokes of much more homogeneous appearance regardless of the location, indicating excellent mutual solubility when cocarbonized (Figs. 5b and c). Although FCC decant oil tends to give larger, or flow, textures, Kafji allowed very homogeneous, medium-mosaic textures. Both cokes contained many pores and fissures. Such appearances are common to those of sponge coke (Fig. 2).

**Coke structure and formation.** The mechanical strength of shot coke may originate from the high-density (low porosity), and fine mosaic texture. The latter characteristic may produce a small number of fissures at the calcination stage, causing high mechanical strength because the fissures often develop along the optical texture.[8, 9]

Real shot coke was not prepared in the present study. But some important similarities of the cokes produced under certain conditions form the characteristic structure of shot coke, and allow some discussion on a possible



**Coarse mosaic** structure of coke produced from Minas resid resembles commercial needle coke (Fig. 3).

scheme of shot coke formation.

The carbonization scheme which determines the optical texture and pore distribution in the coke has been widely discussed in terms of properties and reactivity of mesophase substances at the last stage of carbonization.[11] [12] High viscosity and low devolitization during the final stage, just before the coke solidifies, may give the fine mosaic texture and small number of pores of shot coke.[14]

Hence, the structure of shot coke can be assumed to be built from a group of high-viscosity-coking molecules that have a high coking value because of a lack of solvent-like molecules that reduce the viscosity during carbonization. According to the above consideration, the shot formation is proposed to follow the successive steps which are summarized in Table 2. Some of the steps have been suggested in previous literature.[1] [3] [6]

The segregation of heavy aromatic and polar fractions into a matrix of low dissolving ability is the origin of the shot coke formation. These very viscous and high-coking-yield fractions are precursors of shot coke because they lack the solvent-like fractions.

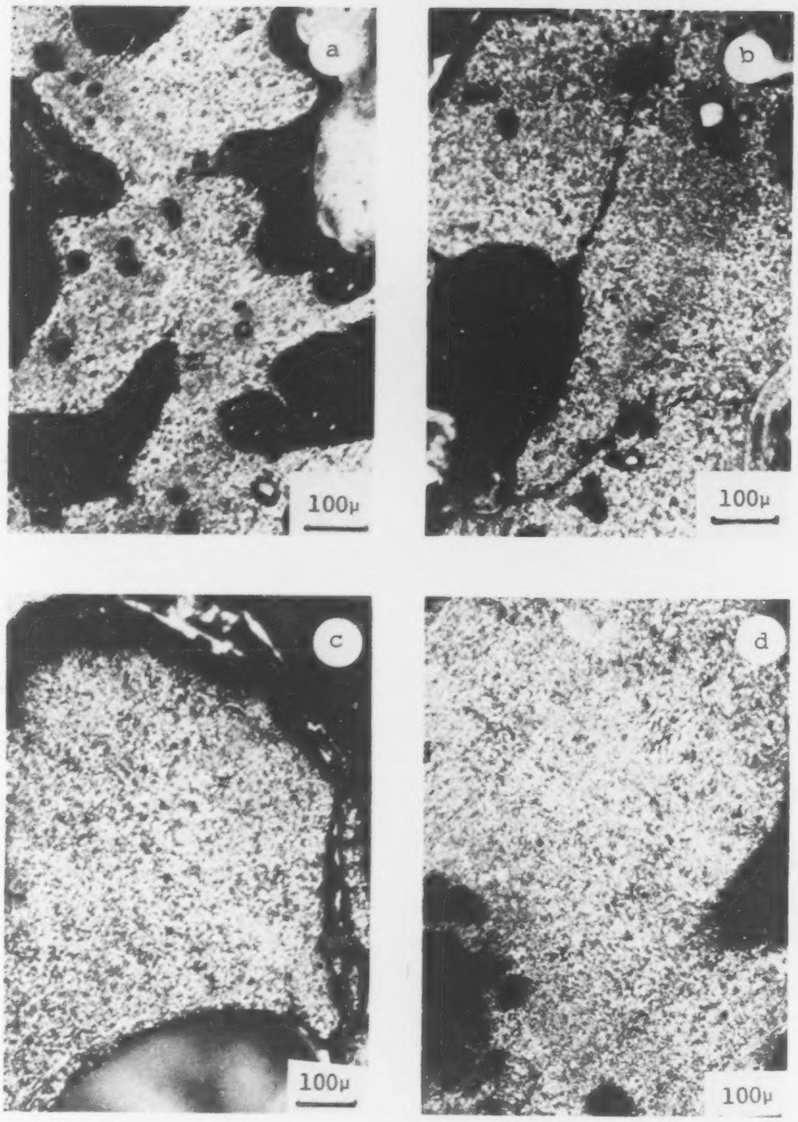
Such segregation may occur even in a single residue after pyrolysis, especially when the devolitization of the solvent fraction is accelerated before the complete coking cycle is completed. This would be expected in two-stage carbonization.

Minas residue, which consists of a large paraffinic fraction and a small very heavy aromatics fraction, probably has long alkyl chains, soluble in the paraffinic fraction. Dealkylation by pyrolysis may decrease the solubility of the paraffinic fraction causing it to be a precursor of shot coke.

Some of the polar fractions can also be precursors of shot coke as the elemental analysis of the shot coke suggested.[1]

Maya residue alone tends to give, in any situation, lump cokes of fine-mosaic and high-density texture similar to shot coke because it consists almost solely of heavy aromatics. But they have little chance of being spherical because the whole residue is so viscous. Maya's high viscosity may also impede smooth and rapid flow in the heating tubes of the coker, requiring some blending.

The blending of residues, which is often performed in a commercial coker, may accelerate or reduce the shot coke formation, depending on



**Increasing carbonization pressures** increased the texture density and reduced the number of pores when Maya resid was carbonized (Fig. 4).

the composition and chemical structure of the residue components. When more of the heavy asphaltene fraction of Maya residue is added to Minas residue, the formation of shot coke is increased because it tends to segregate in the paraffinic matrix of the Minas residue during carbonization.

In contrast, Kafji residue and FCC decant oil, which contain more medium aromatics, can modify the carbonization schemes of heavy aromatic or polar fractions in Maya residue by dissolving them during cocarbonization. The cocarbonization prevents the segregation of the fractions and reduces the viscosity of the carbonizing system through solidification, which enlarges the optical texture and decreases the density.

In these steps, the carbonization pressure is influential on the coke structure since the pressure determines the extent of lighter molecules staying in the carbonization system, and allows the dense packing of carbonizing molecules. A lower pressure quickly eliminates medium aromatics and cracked paraffins, leading to porous cokes.

In contrast, a higher pressure may maintain the distillable aromatics which can increase the optical texture and improve the orientation. Hence, the shot coke may be produced only under medium pressures, probably about 3 to 5 atm where the medium aromatic fraction can be removed. And just such a pressure is required to pass the residual oil rapidly through the heating tubes of a commercial coker.

**Carbonization in commercial coker.** Some characteristic features of coking in the drum of a commercial coker should also be discussed. As is well recognized, the feedstock, which has been pyrolyzed to a certain extent in the heating tube, is sent continuously to the drum, where it is further carbonized into solid cokes.[15]

The carbonization first takes place at the bottom of the drum to form a carbonization zone. Additional feed forms another layer above the first. Such progressive carbonization continues until the drum is filled (Fig. 6).

The carbonization at the bottom may release volatile material and cracked oils to the upper layers with-

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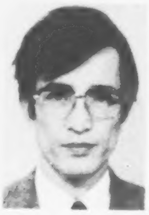

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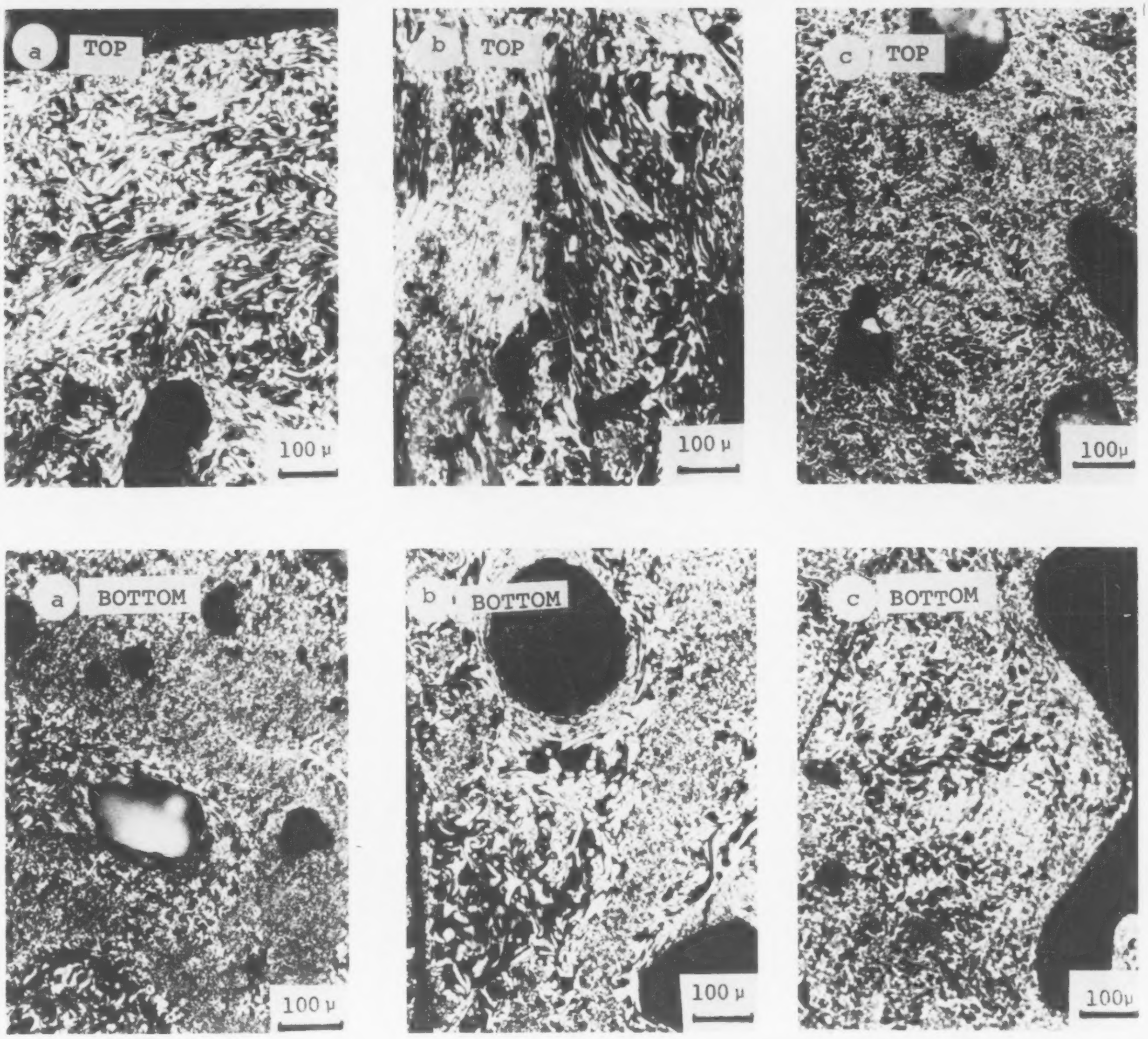
a TOP
100 µ
b TOP
100 µ
c TOP
100µ
a BOTTOM
100 µ
b BOTTOM
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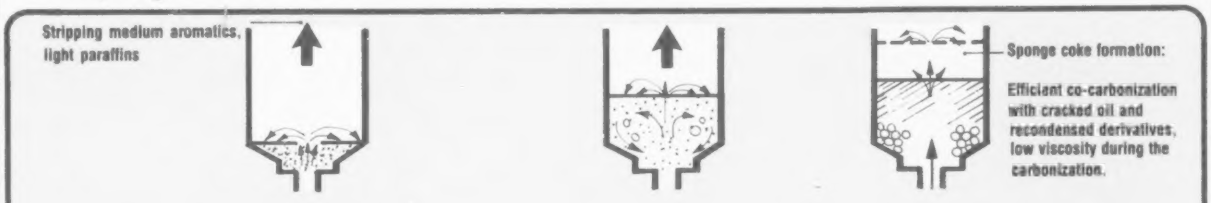
100µ

**Very different textures** were seen between the top and bottom of coke produced from resid blends (Fig. 5).

Fig. 1

## How progressive carbonization takes place in a coke drum


Stripping medium aromatics, light paraffins
Sponge coke formation:
Efficient co-carbonization with cracked oil and recondensed derivatives, low viscosity during the carbonization.

| | | | |
|---|---|---|---|
| **Shot coke formation** | Phase penetration of spherical nulcei of heavy aromatics and oxidized polar fractions in paraffin matrix. | Sphere growth by turbulence, collecting heavy and less-heavy aromatics. | Precipitation of high-viscosity spheres to the bottom or the wall, and matrix evolution. |
| **Shot coke structure** | Random mosaic at the center of sphere. | Concentric orientation of periphery. | Individual or adhered shot cokes. |

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out retaining any of these substances, since the successive feed may pass through the center of the bottom layer. Thus, the lack of an aromatic solvent fraction is most emphasized at the bottom of the drum where more shot cokes have been produced.

A part of the volatile material and cracked oils from the lower layers may be condensed or stay in the upper carbonizing layer for a while to allow a kind of cocarbonization, moderating the viscosity increase and segregation, which decreases the chance of shot coke formation. The cracked oil has a larger dissolving activity because its aromaticity is enhanced through cracking in the drum.

At the top of the drum, the coke becomes porous because the carbonization pressure is low due to thin or nonexistant carbonizing layers.

Since the flow of volatile material through the layers in the drum is not uniform, shot coke has a greater chance to be produced in any part of the drum where the supply of the solvent fraction is retarded.

Another circumstance is related to the recycle of the cracked oil. The oil is usually a medium, aromatic-rich solvent which can work as an excellent carbonization additive to dissolve heavy aromatics of the shot-coke source. Recycle is limited when higher cracked oil yields are expected.

The rapid stream of steam in a commercial coker may increase the cracked oil, but it may also increase the chance of shot coke because the vigorous turbulence of the steam strips the solvent fractions.

**Reduction proposals.** According to the carbonization scheme discussed, the formation of shot coke can be reduced by emphasizing the cocarbonization to prevent the segmentation of heavy aromatic and polar fractions, or to accelerate their dissolution. Such a cocarbonization can be effectively performed by following two major approaches.

The first approach is making adjustments to the feed as follows:

- Selecting the feedstock blend to control the amount of heavy aromatic and polar residues, as well as the solvent fractions of medium aromatics.
- Adding a suitable additive of high dissolving ability against heavy aromatics and polar fractions including hydrogen donors.
- Preheating (like visbreaking) the heavy asphaltene and oxidized fractions to cause their partial degradation.

The second approach is to adjust operating conditions as follows:

- Higher recycle rate
- Higher carbonization pressure
- Slower stripping gas flow
- Uniform gas flow through the entire drum area.

Some of the solutions were described in a previous paper.[3] Very reduced pressure in the drum may also be helpful, although the design of the drum may have to be completely changed.

Such procedures are particularly important at the time of drum switching, when the carbonization continues at the bottom of the drum.

## Acknowledgement

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# Combination of visbreaking and solvent deasphalting boosts gas-oil yields for FCCU feed

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Combined visbreaking and solvent deasphalting, using the Residuum Oil Supercritical Extraction (ROSE) process, increases visbreaker gas-oil yields for fluid catalytic cracking unit (FCCU) feed. And yields can be further increased by adding resin recycle to the combined processes. For comparison, yields of combined processes and visbreaking alone are outlined.

A review of the visbreaking process is included, with a method to calculate conversion in the visbreaker furnace.

For the past several years, refinery crude oil charge has decreased in API gravity and average sulfur, and residuum yields have increased. Future demand for residue will be well below the supply, and it will be necessary to add more bottom of the barrel processing capacity.

Visbreaking cannot solve the residuum imbalance problem completely and it cannot replace the hydroprocessing technology either, but in some particular cases it offers refiners a flexible low cost option to reduce the residuum yields and to reduce the need for relatively expensive cutter stocks. In reviewing the visbreaking process as a residue processing technology, it must be remembered that cutter stock reduction, not destruction of the residue, was the original intent of the process.

Three main objectives can be identified when the visbreaking process is considered:

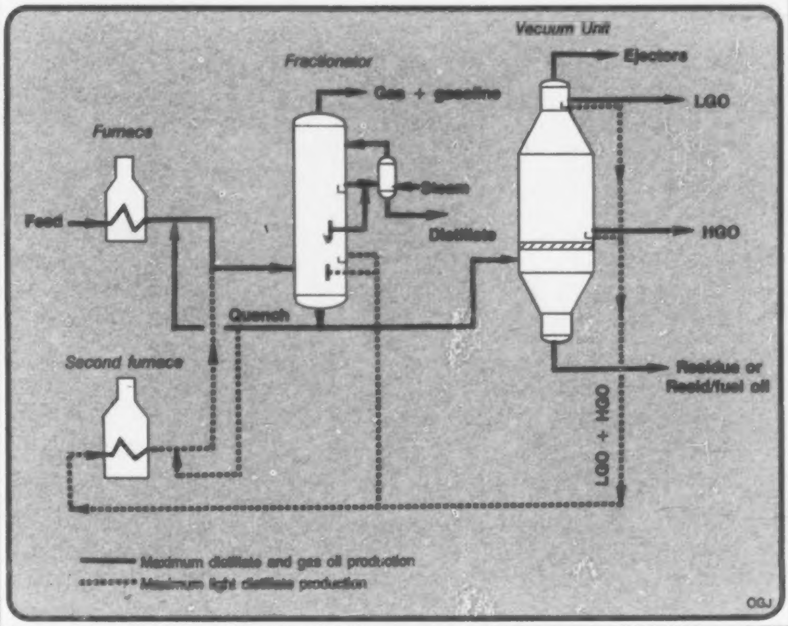
- Reduction of fuel oil production with a simultaneous improvement of its pour point
- Production of maximum light distillate stock
- Production of maximum gas oil feedstock for other conversion processes (FCC).

A careful analysis of the objectives for visbreaking are essential since they might have dramatic input on the processing scheme selected, and upon the overall economics of the project. The analysis must be done bearing in mind that beyond a certain limit of severity, the residue will not remain stable and will tend to form deposits on storage.

**Less fuel oil.** The objective is essentially to reduce the quantity of high value distillates the refiner must add to the high viscosity residue or to propane asphalts in order to produce a heavy fuel oil meeting the commercial viscosity specification. The reduction in viscosity after a certain conversion tends to a limiting value.

Fig. 1

Visbreaking for max. light distil. or distil., gas oil



That means that, while at higher conversion, the production of distillates continues to increase and the viscosity of the 400° F. material goes down, but the viscosity of 650° F. material starts to increase again, probably due to secondary reactions. The conversion at which the gain in viscosity starts to diminish noticeably is sometimes far lower than the maximum conversion permitted by the limit of stability of residue. For instance, if the refiner is interested only in viscosity reduction the chosen conversion might very well be limited to a rather low value.

**Maximum light distillate.** Generally visbreaking is conducted at highest possible severity to produce stable residue. Maximum production of distillate would result in a conversion of 8-12% whereas when viscosity reduction was the only objective, the conversion was limited to somewhat lower value of about 6-7%.

A two coil/furnace arrangement for maximum distillate production can be used; by visbreaking the residuum feed in one furnace and recycling the heavy gas oil produced to the second furnace incorporated into the process unit (Fig. 1).

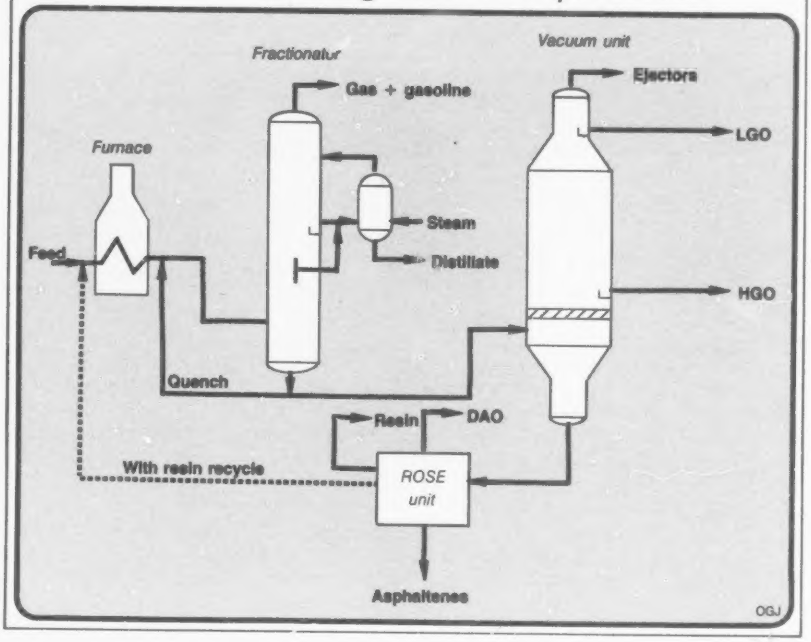
The maximum reduction in the production of the residual fuel through visbreaking can be achieved when alternate disposal exists for the vacuum gas oil cut obtained from a visbreaking unit. The gas oil is usually fed to a secondary conversion unit, generally a catalytic cracker (Fig. 1).

**Visbreaking/solvent deasphalting.** To increase the FCCU feedstock with a visbreaker/solvent deasphalting combination seems to be an attractive alternative with the development and commercialization of the ROSE process.[1] The process represents a significant breakthrough in solvent extraction technology.

The process separates asphaltenes, resins and deasphalted oil and utilizes the supercritical solvent properties to recover the recycle solvent without using the traditional vaporization and condensation steps. This technique made it possible to substantially reduce the energy requirements to recover the recycle solvent. Commer-

Fig. 2

## Combined visbreaking and ROSE processes



cial installations have demonstrated energy savings of 40-50%.

The ROSE process takes advantage of the reverse solubility property, coupled with density differences in oil and solvent to effect a separation between two fluid phases. The supercritical solvent phase is withdrawn overhead from a separating vessel and recycled in the system. Not only the heat of vaporization, but also the energy needed for compression of the vaporized solvent is eliminated.[2-6]

The solvent deasphalting step is used on the visbreaker vacuum tower residuum, and the deasphalted oil is mixed with gas oil and charged to the FCC unit. This deasphalted oil and gas-oil mixture will most probably need hydrotreating before feeding to an FCC unit. This flow scheme of visbreaker/solvent deasphalting is shown in Fig. 2.

**Adding resin recycle.** Visbreaker/solvent deasphalting, together with resin recycle, increases the yield of lighter product.[7] Pilot plant work on this process has been performed and it has been realized that over 50-60% of the high-metal-content resin is converted to gasoline/distillate and low-metal-content deasphalted oil depending on cracking severity.

The theory is that resins stabilize the asphalt in the oil and reduce coke formation in the visbreaker furnace. The alternate flow scheme is shown in Fig. 2.

**Operating variables.** The most important operating variables to all thermal cracking processes are:

- Charge stock properties
- Pressure
- Furnace outlet temperature and residence time

An increase in either of the last two variables results in an increase in visbreaking severity. Increasing the severity increases the gas-plus-gasoline yield and at the same time reduces the viscosity of cracked residue.

Severe cracking conditions may result in an unstable fuel oil as tested by Navy boiler and turbine laboratory tests.

The most important property of visbroken residue is stability. An unstable visbroken residue cannot be improved by blending with even the best cutter stocks and will form sludge during blending and storage.

The typical petroleum residue is a colloidal solution in which the asphaltenes are held in a colloidal suspension in the hydrocarbon phase, the resins and aromatic hydrocarbons acting as peptizing agents. Aromatic cutter stocks (e.g., catalytic cycle oils) are preferred because they don't reduce the stability.

Less aromatic cutter stocks may disturb the colloidal stability between the asphaltenes and the malthenes. This disturbance may cause a flocculation of the asphaltenes and thus sludge formation. Other important properties of visbroken residues are viscosity, sulfur content, Conradson carbon, and asphaltene content.

An increase in processing severity results in a marked decrease in the cutter oil requirement and decrease in the yield of No. 6 fuel oil. At the higher severities, further cutter stock savings are not realized, but fuel oil yields are reduced by converting visbroken tar to distillate, naphtha, and gas.

Operating pressures for visbreakers are in the range of 150 to 400 psig, depending on whether the cracking is done in the furnace or a combination of furnace and soaking drum. Temperature is the major factor controlling the rate of cracking/visbreaking reactions and, together with reaction time, governs the extent of conversion that will take place in any given equipment.

The fundamental basis of cracking is that it is a time-temperature function, and to a considerable extent these are interchangeable. Cracking reactions are endothermic, hence heat of cracking should be taken into account for designing the furnace. It is normally accepted that cracking starts at 800° F. for heavy oils.

**Visbreaking yields.** A majority of the experts correlate their yields: debutanized gasoline against gas, distillate, gas oil, and residue. Here, yields are correlated at maximum severity against pentane insolubles.

Asphaltenes are insoluble in n-pentane and other noncyclic light hydrocarbons. Some experts correlate visbreaking yields with modified naphtha insolubles (MNI).

Sediment by extraction is another variable together with pentane insolubles, which is used for correlating visbreaking yields. Pentane insolubles can be correlated by Conradson carbon or ring-and-ball softening point.

Fig. 3 shows a correlation of Conradson carbon and ring-and-ball softening point to pentane insolubles. Visbreaking yields of gas, naphtha, distillate and gas oil against pentane insolubles are given in Figs. 4, 5, and 6, respectively. Fig. 7 gives the distribution of sulfur in products against sulfur in the feed.

These correlations are for maximum severity case only. The cracking severity is usually expressed as conversion which is defined as the yield of light products, i.e., gas + gasoline.

**Comparison of typical yields.** Table 1 gives typical yields for Cold Lake crude for visbreaking, visbreaking/ROSE combination, and visbreaking/ROSE combination with resin recycle. These yields show the advantages of the addition of ROSE to visbreaking and resin recycle.

Table 1

## Typical yields for Cold Lake crude, 10.8° API

| | Visbreaking, wt % | Visbreaking + ROSE, wt % | Visbreaking + ROSE + Resin cycle, wt % |
|---|---|---|---|
| Charge | 100.0 | 100.0 | 100.0 |
| **Products** | | | |
| $C_3$- | 1.09 | 1.09 | 1.26 |
| $C_4$ – 400 F. | 8.5 | 8.5 | 9.3 |
| 400-650 | 22.8 | 22.8 | 23.21 |
| 650-950 F. | 25.0 | 25.0 | 24.31 |
| 950 F. + * | 42.61 | 42.61 | 41.92 |
| DAO | — | 18.9 | 21.21 |
| Resin | — | 5.6 | — |
| Asphaltene | — | 18.11 | 20.71 |
| | 100.0 | 100.0 | 100.0 |
| Conversion to 950° F. + DAO wt % on feed | 57.39 | 76.29 | 79.29 |

* Feed to ROSE unit

**Furnace and soaker design.** It is customary to use box-type furnaces and a minimum cold oil velocity of 5.5 to 6.0 fps. In the radiant section, a maximum heat flux in the range of 10,000 to 11,000 BTU/hr-ft$^2$, and for the soaking section, maximum heat flux of 5,000 to 6,000 BTU/hr-ft$^2$ is recommended.

The furnace must be designed to give the required soaking factor and crack per pass. Step-by-step calculations in small increments of furnace length should be performed to check the conversion and crack per pass.

Thermal cracking can be attained by heating the feed to high temperature in the furnace. Alternatively, it can also be achieved by heating to a lower temperature in the furnace and then let the cracking proceed in a soaker drum with a longer residence time as suggested by M. Akbar, et al.[8]

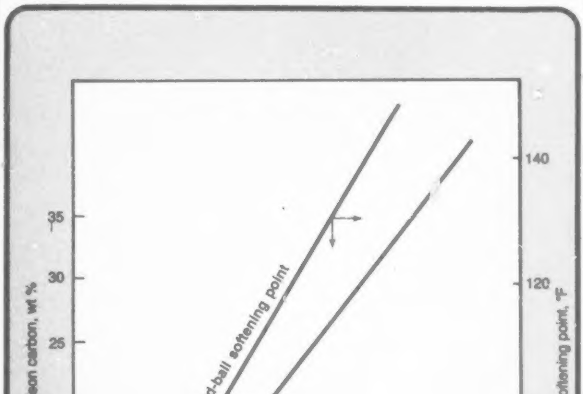
The advantages with soaker drum cracking are lower capital cost, lower fuel consumption, and longer on-stream times. Soaker drums normally with upward flow are used and back-mixing should be avoided.

It has been reported that residence time for the vapor phase in the soaker drum is less than 1/10 of that of the liquid phase, so further cracking of vapor products is lower.[8] In soaker cracking, the yield of gas is marginally lower than in furnace cracking which is a desirable selectivity for a visbreaker.

The advantages of soaker cracking are a smaller furnace, less waste heat recovery equipment, lower pressure drop through the furnace, lower fuel use, longer run length before decoking, high on-stream time, and lower outlet temperature from the furnace.

Fig. 3

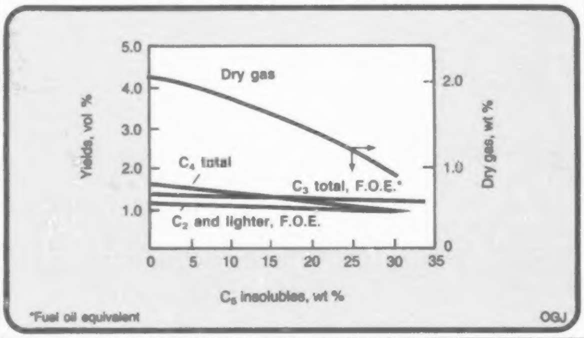
## Con carbon and softening*



* correlated to $C_5$ insolubles

Fig. 4

## Yields of $C_4$ and lighter components



*Fuel oil equivalent

Fig. 5

## Yields of naphtha, distillate, gas oil

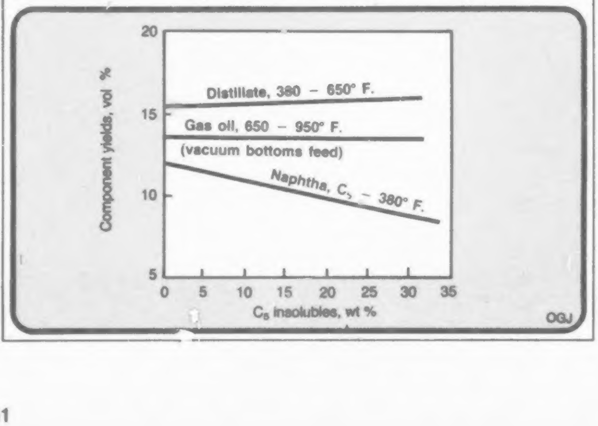


Table 2

## Interpolation of API enthalpy data

| | Weight fraction X | H @ 820° F. Btu/lb | H @ 830° F. Btu/lb |
|---|---|---|---|
| Gas | 0.0012 | 790 | 795 |
| Gasoline | 0.0033 | 685 | 690 |
| Oil | 0.9955 | 540<br>(540.8) | 549<br>(549.8) |

Temperature @ 546.1 BTU/lb enthalpy = 826° F. i.e., 1,286° R.

**Sample conversion calculations.** At the start of the calculations, pressure drop for the furnace is assumed and from it inlet pressure can be ascertained.

Furnace outlet temperature is also assumed so as to give the required conversion. From outlet temperature, product composition, and inlet temperature of the oil, the furnace duty can be calculated.

Tube size and the number of passes are determined to give a desired cold oil velocity as given in guide lines. From the desired heat fluxes, the furnace is designed to perform the duty calculated. Furnace surface area and volume is used to calculate the conversion.

Feed is preheated in the convection section of the furnace to below 800° F. From the average heat flux, determine how much surface area and volume of the radiant section is used to reach the 800° F. point. Find the surface area and volume available for cracking, i.e., above 800° F.

Inlet data:

- Total surface area of radiant section = 9,216 sq ft
- Total heat duty of furnace radiant section = $60.62 \times 10^6$BTU/hr
- Flow = 376,000 lb/hr
- Feed gravity = 7.0° API
- UOP K = 11.7
- Total conversion required = 5.4 wt % (gas + gasoline)
- Inlet pressure = 262.7 psia
- Inlet mixture density = 41.5 lb/cu ft @ 800° F.
- Molecular weights:
  Gas = 25.8; gasoline = 115; heat of cracking = 350 BTU/lb
- Furnace tubes: (4-pass furnace)
  OD = 4 in.
  ID = 3.25 in.
- Volume available for cracking = 481.84 cu ft
- Surface area available for cracking = 8,759 sq ft

Incremental calculations are run on increasing fractions of the surface area available for cracking. They begin at 0.2 of the total surface area and proceed at increments of 0.2, ending at 1.0 of the total surface area (i.e., calculations are run at 0.2, 0.4, 0.6, 0.8, and 1.0 times the total).

First calculate average heat flux in radiant section: $60.62 \times 10^6/9{,}216$ = 6,580 BTU/hr/sq ft.

The heat input to the surface area fraction (Z = 0.2) is calculated by:

$$\frac{8{,}759 \times 0.2 \times 6{,}580}{376{,}000} = 30.7 \text{ BTU/lb}$$

The conversion for the surface area fraction is assumed at 0.45 wt % or 0.0045. The enthalpy is then determined at the surface area fraction by adding the endothermic and exothermic heats:

Enthalpy at 800° F. = 517 BTU/lb

Heat input to Z = 0.2 = 30.7 BTU/lb

Heat of cracking, $350 \times 0.0045 = -1.6$ BTU/lb

Enthalpy of fluid at Z = 0.2 = 546.1 BTU/lb

From the above, the temperature of the charge at the fluid enthalpy is determined by interpolating values of enthalpy from API charts. The weight fractions of gas, gasoline, and oil are determined from Figs. 4, 5, 6 and are: gas, 0.0012; gasoline, 0.0033; and oil, 0.9955 (Table 2).

The resulting temperature is 826° F. or 1,286° R.

The pressure at Z = 0.2 is determined by assuming a pressure drop for the fraction.

The pressure drop is assumed at 14.7 psi, therefore, the pressure is 248 psia.

The volumes of the components are calculated as follows and are tabulated in Table 3.

Fig. 6

Yields of 650° F. + and 950° F. +

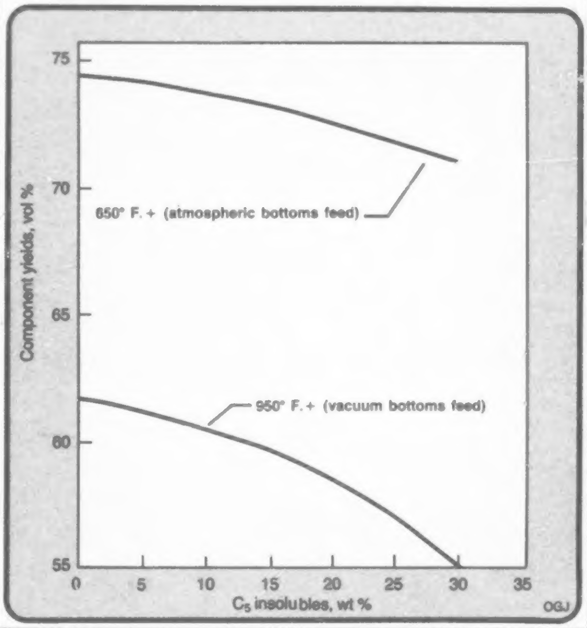


Fig. 7

Product sulfur content

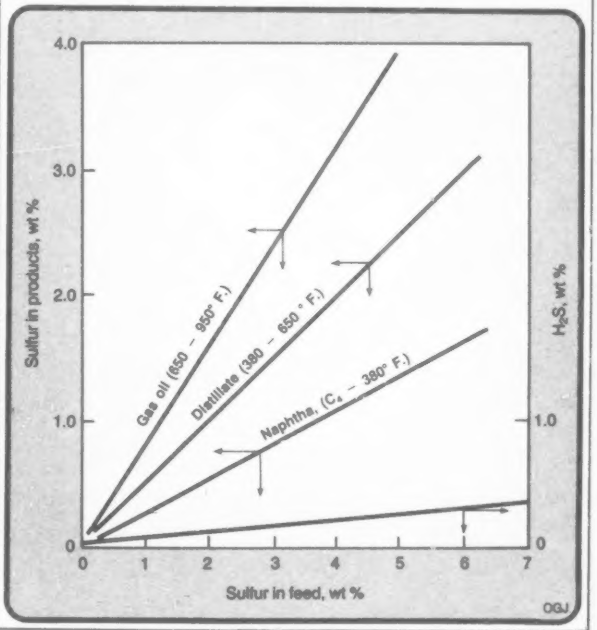


Table 3

## Data for volume calculations

| | Weight fraction, X | Critical temp, $T_C$, °R. | Critical press., $P_C$, psia | Reduced temp, Tr | Reduced press., Pr | μ | w | v | xv |
|---|---|---|---|---|---|---|---|---|---|
| Gas | 0.0012 | 510 | 750 | 2.5 | 0.33 | 1.0 | — | 2.16 | 0.0026 |
| Gasoline | 0.0033 | 1035 | 562 | 1.2 | 0.44 | 0.9 | — | 0.43 | 0.0014 |
| Oil | 0.9955 | 1360 | 150 | 0.9 | 1.65 | — | 0.09 | 0.024 | 0.0239 |
| | | | | | | | | (Total) | *0.0279 |

$^*\Sigma_{xv} = 1/\rho_2 = 35.8$

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Lutz has BS and MS degrees in chemical engineering from the University of Louisville.

$$V_{gas} = \frac{1544 \times \mu T}{144 \times PM}$$

$$= \frac{1544 \times 1.0 \times 1286}{144 \times 248 \times 25.8}$$

$$= 2.16 \text{ cu ft/lb}$$

$$V_{gasoline} = \frac{1544 \times 0.9 \times 1286}{144 \times 248 \times 25.8}$$

$$= 0.43 \text{ cu ft/lb}$$

$$V_{oil} = \left[\frac{\omega \text{ @ } 60° \text{ F.}}{\text{SG @ } 60° \text{ F.} \times \omega \text{ @ temp}}\right]$$

$$\frac{1}{62.4} = \frac{0.14}{1.022 \times 0.09 \times 62.4}$$

$$= 0.024 \text{ cu ft/lb}$$

where:

V = Volume, μ = compressibility factor, ω = Expansion factor, SG = Specific gravity of oil, and 1544 = Universal gas constant.

From these calculations the density, $\rho_2$ of the mixture at Z = 0.2 ($\rho_2$ = 35.8) is calculated from data in Table 3. The average density of the mixture at Z = 0.2 is calculated from the above $\rho_2$ and the given $\rho_1$ by:

$$\rho_{av} = \frac{\rho_1 - \rho_2}{\ln \dfrac{\rho_1}{\rho_2}} = \frac{41.5 - 35.8}{\ln \dfrac{41.5}{35.8}}$$

$$= 38.6 \text{ lb/cu ft}$$

The actual pressure drop (ΔP) for the fraction of the surface area, Z = 0.2 is calculated by:

$$\Delta P = \frac{2f\,G^2L}{144\,g\,D\rho_{a_v}}$$

where:

$$G = \frac{\text{Flow x}}{\text{No. of passes}}\;\frac{1}{3600} \times$$

$$\frac{1}{\text{cross section of tube}} = \frac{376{,}000}{4}$$

$$\times \frac{1}{3600} \times \frac{1}{0.05758}$$

$$= 453.58 \text{ lb/sec-sq ft}$$

f = 0.004

L = Tube in radiant section, above 800° F. = 2091 ft/pass

D = Tube ID = 3.25 in.

g = Gravitation constant = 32.2 ft/$\text{sec}^2$

Therefore, the pressure drop is:

$$\Delta P = \frac{2 \times 0.004 \times (453.48)^2 \times 2091 \times 0.2}{32.2 \times \dfrac{3.25}{12} \times 38.6 \times 144}$$

$$= 14.3 \text{ psia}$$

The actual pressure of the mixture at Z = 0.2 is (262.7 − 14.3) = 248.4 psia which is sufficiently close to the assumed 248 psia. The average temperature at Z = 0.2 is (800 + 826)/2 = 813° F.

Finally, the conversion at Z = 0.2 can be calculated by a first order reaction; the reaction is $\ln a/(a - x) = kt$

Where a = 1, weight fraction of oil in feedstock and t = residence time.

The conversion at Z = 0.2 is:

$$\text{Conversion} = kt$$

where: t = Residence time, sec

The residence time is calculated from:

$$t = \frac{\text{furnace volume at } Z = 0.2}{\text{volumetric flow}}$$

where:

Furnace volume = vol available for cracking × Z

$$= 481.84 \times 0.2 = 96.368 \text{ cu ft}$$

$$\text{Volumetric flow} = \frac{376{,}000}{3600} \times \frac{1}{38.6}$$

$$= 2.71 \text{ cu ft/sec}$$

$$\text{The residence time, } t = \frac{96.368}{2.71}$$

$$= 35.5 \text{ sec}$$

In this calculation, k = $1.4 \times 10^{-4}$ $\text{sec}^{-1}$ (from Nelson[9]), but normally the value of k will be taken from pilot plant data. Therefore, the actual conversion for Z = 0.2 is:

Conversion = $1.4 \times 10^{-4} \times 35.5$ = 0.0049

The result is sufficiently close to the assumed value of 0.0045. The preceeding calculations are repeated for the increasing increments of the available surface area until Z = 1.0. When the calculated conversion reaches or exceeds the desired conversion, the furnace design parameters are satisfactory. The same calculation procedure may be used to calculate the conversion in the soaker drum.

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# Freon or propane: New design methods give a choice for small gas-processing plants

**Don L. Love**
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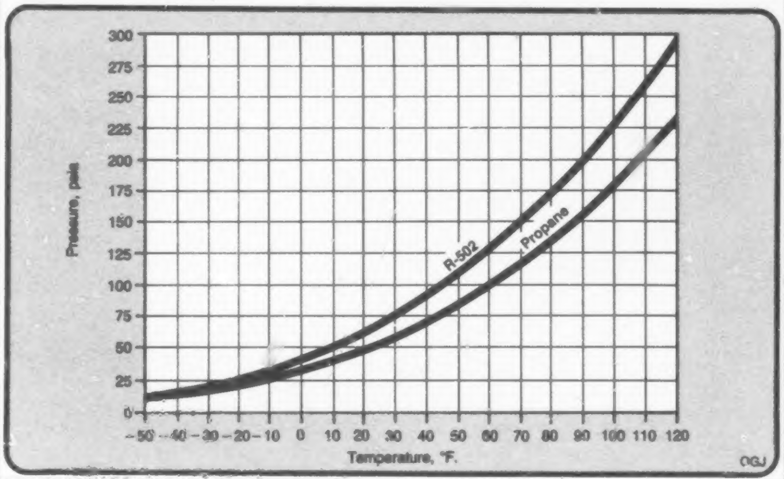
Fig. 1

Saturation pressure vs. temperature



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Propane, and sometimes ammonia, have been the major refrigerants considered for refrigeration in liquid extraction plants. Freon was considered only for automotive and building air conditioning. With modular plants on skids becoming more popular for small volume applications, less-expensive equipment approaches are required to economically justify these small projects.

Commercial and residential design methods can be used for refrigerated liquid extraction. They can significantly reduce the cost, compared to propane, for small volume applications.

Although it appears to be a simple substitution of Freon for propane, there are many complications in using Freon. They include major changes in materials, and in chiller and compressor design.

Love Process Engineering Inc. (LPE) has conducted extensive research on Freon and propane plants for modular applications. This article will not discuss detailed design requirements, but compare Freon and propane in the initial selection of project development for small volume applications.

**Physical difference.** Although there is a basic design for refrigerated liquid extraction plants, there is a vast difference in design of the refrigeration section:

- Freon plants are designed for flow in the tubes. Propane plants are designed for flow in the shell.

Freon in the tubes allows Freon oil to sweep through the exchanger. On the shell side, the oil will collect at baffles and significantly reduce the transfer coefficient. Freon compressor oil partially vaporizes, approximately 5-10%, and condenses with the Freon. It is virtually impossible to prevent oil contamination in the chiller. LPE film coefficient research has permitted development of the calculation procedures necessary to allow for oil in the chiller.

In addition, Freon has a high liquid density, compared to propane. Consequently, liquid Freon requires a larger driving force (pressure drop) to clear a flooded tube. Since the pressure drop is extremely small in the tubes, the tube sheet should be designed to prevent excessive liquid Freon buildup in low areas.

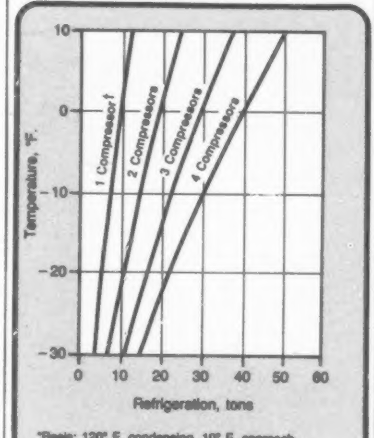
- Freon plants may have refrigeration and process compressors on the same skid. Propane compressors are externally mounted, on separate skids.
- Refrigeration piping for Freon is hard-drawn copper. Carbon steel is used for propane. Steel is extremely difficult to seal from Freon leakage. The copper must be soldered with a high grade of silver.
- Electric-motor-driven compressors are preferred for Freon.

In a typical Freon plant, the entire process may be on one skid. Often, insurance requirements will force the direct-fired glycol reconcentrator to be put on a separate skid. The refrigeration compressors and control panel are mounted in a building on a skid; the condenser is mounted over the building.

Typical propane refrigeration plants have the propane compressor, propane condenser, and the process on separate skids. For this example, the propane chiller is a standard shell-and-tube exchanger with the propane in the shell flooded by an elevated vessel, maintaining liquid level. This is the same principle as a kettle-type chiller, but has a reduced cost for small applications.

Fig. 2

Temp. vs. tonnage*



*Basis: 120° F. condensing, 10° F. approach
†Model 6DL1-2700-TSK

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A refrigeration system using Freon is more complicated than a propane system. Extreme protection is required to keep liquid slugs from the compressor suction and to maintain proper lubrication to prevent compressor failures.

**Freon type.** Most Freon applications use Freon R-502, which is very close to propane (Fig. 1). At the chiller, the Freon and propane are very close in saturation pressure. At the condensing temperature (120° F.), the condensing

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From a presentation at the Gas Processors Association, Panhandle Plains Regional Meeting, Amarillo, Tex., Oct. 10, 1985.

Table 1

## Cost comparison

| | Freon | Propane |
|---|---|---|
| Inlet, Mscfd | 3,000 | 3,000 |
| Chiller temperature, °F. | −13 | −25 |
| Tons refrigeration | 24.5 | 28.3 |
| Liquid recovery, gal/day | 4,670 | 5,464 |
| RVP | 175 | 207 |
| Fuel, Mscfd | 9 | 27 |
| Sales, Mscfd | 2,845 | 2,793 |
| Plant type | Freon (GP 20) | Propane (GP) |
| Refrigeration compressor | Four, semi-hermetically sealed, in parallel | One, gas-engine driven |
| Capital investment, $ | | |
| Plant | 170,000 | 160,000 |
| Refrigeration compressor | (included with plant) | 80,000 |
| Subtotal | 170,000 | 110,500 |
| Job site installation (see Table 2) | 90,000 | 110,500 |
| Total | 260,000 | 350,500 |
| Estimated operating cost/month (exclusive of labor), $ | | |
| Refrigeration make-up | *100 | 300 |
| Lubricants | Nil | 200 |
| Electrical ($0.06/kw) | 2,600 | 500 |
| Contingency | 300 | 300 |
| Total | 3,000 | 1,300 |

* Average

Table 2

## Job site costs

| | Freon | Propane |
|---|---|---|
| Storage, 30,000 gal | $24,000 | $24,000 |
| Load pump with hoses | 3,500 | 3,500 |
| Foundations | 10,000 | 14,000 |
| Insulation | —— | 6,000 |
| Pipe, valves, and fittings | 8,500 | 14,000 |
| Construction contractor | 15,000 | 25,000 |
| Electrical | 10,000 | 5,000 |
| Contingencies | 5,000 | 5,000 |
| Engineering, project management, etc. | 8,000 | 8,000 |
| Roads, etc. | 6,000 | 6,000 |
| Total | 90,000 | 110,500 |

Table 3

## Economic evaluation format

Plant balance:
1. Gas rate, Mscfd
2. Liquids recovered, gal/day
3. Sales gas, Mscfd (No. 1 − No. 2 x 0.032 − A*)

Increase in income:
4. Price of gas, $/Mscf
5. Price of liquid, $/gal
6. Value of inlet gas (No. 4 x No. 1)
7. Value of sales gas (No. 4 x No. 3)
8. Value of liquid ($5 x No. 2)
9. Increase in income/month (No. 7 + No. 8) x 30)

*A = 0.005 x No. 2 for propane and No. 5 for Freon.

Table 4

## Overall comparison

| | Freon | Propane |
|---|---|---|
| Gas rates, Mscfd | 200 to 5,000 | 1,000 and greater |
| Refrigeration, tons | 5 to 30 | 30 and greater |
| Chiller temperature, °F | −5 to −20 | −20 to −35 |
| Refrigeration material | Copper | Carbon steel |
| Chiller design | Freon in tubes | Propane in shell |
| Compressors | Semi-hermetically sealed, electric driven | Gas or electric driven |
| Refrigeration make-up | Nil* | 200 gal/month and greater |
| Recovery of liquids | Less | More |
| Plant cost | Less | About 30% more |
| Installation | Less | About 20% more |
| Operating cost | About 50% more | Less |
| Electrical | About 3 times more | Less |
| Fuel | Less | About 10 times more |

*Unless unusual leak is present

pressure is higher for Freon than propane. As a result, the Freon compressors will have a slightly higher suction pressure, with a much larger discharge pressure, 294 psia for Freon and 249 psia for a propane.

The rise in compression temperature is higher for Freon than propane. Thus discharge temperature of the Freon compressors should always be less than 220° F. to avoid cracking. Therefore, the colder the suction temperature for the Freon, the less chance of too high a discharge temperature.

**Refrigeration loads.** Freon plants have the advantage of substantially less initial investment. They are limited, however, in refrigeration load because of the practicability of using small compressors. As a rule of thumb, the maximum refrigeration load is approximately 30 tons, before it becomes impractical to use Freon. A propane-based plant should be used for 30-ton loads and larger.

In addition, if electricity is not available, propane compressors are more desirable. The driver can be gas powered and a hydraulic system used to drive pumps and fans.

**Compressor comparison.** For small applications, the Freon compressor is electric-motor driven, and semi-hermetically sealed to prevent Freon leaks. The cost of Freon is approximately six times greater than that of propane. The propane compressor may be electric motor or gas-engine driven, with a coupling or V-belt between compressor and driver.

The largest semi-hermetically sealed compressor driver is generally 30 bhp. For most applications, the Freon compressors are installed in parallel service, to a maximum of four.

Fig. 2 presents a typical relationship of Freon compressor refrigeration load to chiller temperature. As expected, the lower the chiller temperature, the higher the refrigeration demand. From this analysis, the maximum number of compressors can be determined.

**Refrigeration efficiency.** Propane refrigeration has a better recovery. This is because the propane-based refrigeration plant has no upper limit to the refrigeration load and the chiller temperature can be anywhere from −20° F. to −35° F.

Freon-based plants, however, do not have as low a chiller temperature, except at very low refrigeration load conditions. Freon plant chiller temperatures generally range from −5° F. to −20° F.

The lowest recommended chiller temperature is −25° F. using standard A-214 exchanger tubes and A-106B pipe for the shell. Temperatures to −35° F. may be used, with caution given to the limits of the stress on the steel. If impact steel (A-300) is used at a lower temperature, the cost is increased.

The principal reason for not going any lower than a −35° F. chiller temperature is to prevent the suction pressure of the propane compressor from being in vacuum.

For −35° F., the compressor suction will be approximately 1.5 psig, depending upon the chiller's temperature approach.

**Cost comparison.** In a cost compar-

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ison (Table 1), the propane-based plant will be substantially more because of the refrigeration compressor. If it is leased, the investment will be about the same as a Freon plant. But the operating cost will be higher for propane because of the lease payments. Comparing operating costs, the major difference is that Freon-based units have a high electrical load. Propane-based units usually have a high fuel consumption, with less sales gas. In addition, propane units have a consistent propane consumption.

The installation cost (Table 2) for the propane-based plant is about 20% higher than a Freon-based plant because of additional piping, field insulation, and additional foundations. There is, however, a lower investment for electrical installation for propane. In fact, the propane-based plant can be totally free of electrical requirements by using an hydraulic system for the pumps and cooling fans.

**Compressor leasing.** Some compressor vendors will lease the propane compressor, but are reluctant to do so because of the possibility that it will not be compatible in other applications. However, they are beginning to recognize that a standard, two-stage gas compressor can be slightly modified for propane refrigeration service. Since the propane compressors do not need interstage cooling for this use, the coolers can be left on the skid for standard gas applications, and temporary bypass piping installed. Other changes are rather minor.

**Economic evaluation.** Table 3 is a format for economic evaluation. Although the investment is greater for the propane plant, the increased recovery and decreased operating cost may justify the propane-based unit.

It is also worth considering the loss in income from gas sales and fuel usage. Most liquid spot market prices range from $0.40 to $0.45/gal, less transportation and fractionation fees. Most fractionation fees range from $0.03 to $0.06/gal, depending upon the area or distance to a fractionation facility.

A reasonable payout ranges from 12 to 24 months, before taxes. There are many applications, however, when the payout is less than 12 months, especially when the gas value exceeds 1,200 BTU/scf.

From economic analyses of numerous projects, the break-even point for most small projects may be related to a minimum liquid recovery of 800 gal/day.

**Overall comparison.** In an overall comparison of Freon and propane-based plants (Table 4), the Freon plant is less expensive for small applications, less than 30 tons of refrigeration, but does have a higher operating cost. In addition, Freon refrigeration has less overall recovery than propane refrigeration.

For small projects, the Freon plant is easier to justify for liquid recoveries of 800 gal/day to 5,000 gal/day. Otherwise, the propane plant is generally more economically feasible. ▪

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# In-line blending

**William E. Morris**
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Refiners can improve the economics of their gasoline-blending operations and octane and volatility analyses by using in-line blending procedures and on-line specification analysis.

The Environmental Protection Agency's current lead content rules have decreased refiners' blend options to meet octane specifications, and tigher vapor pressure controls that may be imposed nationwide and in force in some areas, will restrict refiners' use of butane to control Rvp.

In-line blending operations allow refiners to blend gasoline components closer to the specification, reducing the excess amount of high octane material needed to ensure proper octane level of the finished gasoline. If gasoline Rvp is restricted, refiners will want to blend as much low-cost butane without exceeding the Rvp limits.

Improvements in blending and analysis equipment have decreased the relative costs and improved the performance of the equipment. And although, during the last 20 years in-line blending systems have been installed in about 100 refineries in the U.S. and Canada, some of these refineries are not making full use of the economic advantages offered.

Refiners that do not have in-line blending should consider making a serious evaluation even though a project may have been turned down in the past. Refiners who already have in-line blending might want to reevaluate their equipment and procedures.

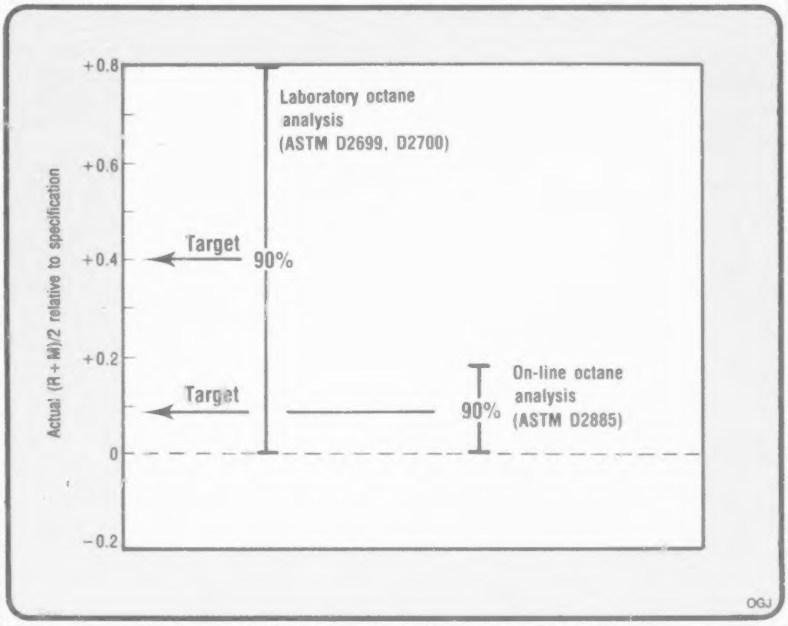
**Advantages.** Reduction in inventory can be made because blends are prepared more quickly. In batch blending, time is required to recirculate blends, obtain analytical data, and reblend. The longer the unfinished blends are held, the greater the inventory must be.

With in-line blending, blends are finished as they are made. The inventory is reduced, and the reduced inventory consists primarily of components rather than finished blends. The reduction of inventory gives a one-time saving that can be expected to pay roughly half the cost of the in-line blending system.

Decreased tankage requirements result from the reduction in inventory. This translates to greater flexibility of

# and on-line analysis offer advantages

Variation of octane when result is on target



refinery operations. If additional tankage would otherwise be needed, installation of in-line blending can save the cost of one or more tanks.

Decrease in quality give-away is generally the largest pay-off of in-line blending. With a continuous octane analyzer, a target only 0.1 octane above specification will give a high level of assurance of meeting the specification. With batch blending, the target must be about 0.4 octane above specification to give the same assurance of meeting the specification.

With a continuous Reid vapor pressure (Rvp) analyzer, a target of 0.1 lb below Rvp specification will give a high level of assurance that the specification will not be exceeded. With batch blending, the variability of Rvp is likely to be larger and, consequently, the Rvp target needs to be lower. Otherwise, too many blends must be reblended to bring down the Rvp.

With a lower target, less butane will be used with batch blending. The importance of Rvp blending is increased by government regulations requiring lower Rvp. With lower allowable Rvp, the price of butane decreases thereby increasing the incentive to blend as close to target as possible, using as much butane as possible.

For the larger refineries, the first year's saving due to inventory reduction and decreased quality give-away can be expected to pay off the cost of the in-line blending system including the continuous octane and volatility analyzers. Generally, the economics are less favorable for smaller refineries, but in-line blending systems are being planned for refineries in the 50,000 b/d range.

For refineries smaller than 50,000 b/d, it may still be economical to install in-line blending. But just an evaluation of gasoline blending and testing procedures can result in profitable improvements even if in-line blending is not installed.

**Octane giveaway.** Refiners doing batch blending ususally have difficulty in making an accurate evaluation of the decrease in octane quality giveaway that an in-line blending system will provide. With octane, as with any specification that is limiting, the goal should be to meet the specification almost all the time. On this basis, the target must be far enough within specification so that only a small percentage of the product actually fails to meet the specification.

With batch blending, the target should be from 0.3 to 0.5 octane above the specification depending upon the situation. With limited tankage it may be necessary to "shoot high" because of the unpleasant consequences of making a blend below specification. In this situation, blends may be shipped well above specification because there simply isn't time to make an adjustment.

With batch blending, where sufficient tankage is available, a large amount of reblending can be expected. This results because accurate octanes on the gasoline components are seldom available, octane blending equations may not be accurate, and octane measurement inaccuracies affect results no matter how much reblending is done. And many refineries do not have experienced octane engine operators for organizational reasons.

Even with experienced operators, laboratory octane tests are subject to appreciable error because of the behavior of the knock test engine. When a knock test engine is running without being touched, the knock intensity varies for reasons we do not need to discuss here.

Consequently, when the same gasoline is tested repeatedly, the results will vary. This variation is called repeatability. An average of several results will give a better answer, but time may not permit repeat testing.

There is another source of variation that is not affected by repeat testing. That source is the engine effect. Averages of many tests in each of two engines may be appreciably different, primarily due to differences in combustion chamber deposits.

The repeatability plus the engine effect is called reproducibility which refers to results obtained in different engines. The reproducibility standard deviation is about ±0.3 octane for research, ±0.4 octane for motor, and ±0.25 for (R+M)/2, based on single octane measurements.

On this basis, the target octane must be 0.4 above specification in order to have 95% odds that the actual octane is equal to or above the specification. The variance of (R+M)/2 is as follows:

$(0.5)^2(0.3)^2 + (0.5)^2(0.4)^2 = 0.0625$

The standard deviation of (R+M)/2 is: 0.0625 = 0.25 octane. There is a

90% chance that the actual octane number will be within 1.64 standard deviations of the result obtained, or within 1.64 × 0.25 = 0.41 octane.

There is a 5% chance that the actual octane number will be more than 0.41 octane below the result obtained. Consequently, if the result is 0.41 octane above specification, there is a 95% chance that the actual octane is equal to or above the specification.

This should be taken into account when estimating the advantage of in-line blending with on-line octane analyzers. However, refiners usually look at the measurements of the octanes of blends when estimating octane giveaway and the potential advantage of in-line blending. This results in an underestimate of octane variability from batch to batch.

With batch blending, there is a 50:50 chance that the octane measurement error will compensate for the blend error. In one case, the actual octane of the blend will be high and the octane measurement low. The result will look like the blend is on target and it will be shipped with octane giveaway.

In another case, the actual octane of the blend will be low but the measurement high. The result will look like the blend is on target, and it will be shipped at below specification.

There is a 50:50 chance that the octane error and the blend error will be additive. If so, a reblend will probably be made and, again, there is a 50:50 chance of compensating errors.

The greater the number of reblends the greater the chance that the blend will be shipped with an underestimate of its deviation from the octane target. This bias results from the nature of batch blending.

Consequently, the octane advantage of in-line blending is usually underestimated. An unbiased independent audit of octane quality would be required to obtain an accurate measure of octane quality variation with batch blending.

**Octane analyzers.** Octane variability from batch to batch can of course be improved, but it cannot approach that achieved by on-line octane analyzers. Why are on-line octane analyzers so much better?

The key to accurate octanes using on-line analyzers (ASTM D-2885) is calibration of standard fuels which are average composition gasolines. By obtaining octanes in 25 different research and motor octane engines, the (R+M)/2 standard deviation is only 0.05 octane. Standard deviation of an average is the standard deviation of an individual result divided by the square root of the number of results in the average, or 0.25/25 = 0.05.

## The author...

**Morris**

William E. Morris is a consultant located in Wilmington, Del., with experience in gasoline manufacture, blending, testing, specifications, and applied statistics. He worked for 32 years at the Du-Pont Co. where he conceived and developed technical service programs that are provided to petroleum refiners. He has been active in ASTM and Coordinating Research Council committees and has authored 26 papers and publications in the field of gasoline quality.

In practice, standard fuels are kept in cold storage and used only to obtain very accurate octane calibrations of large batches of prototype fuel. The prototype fuel is very similar to the standard fuel, and to the gasoline product being blended.

These similarities almost eliminate the previously mentioned engine effect because standard fuel, prototype fuel, and product respond almost identically to changes in combustion chamber deposits and other engine conditions. The repeatability error is essentially eliminated because the product being blended is compared with the prototype over and over.

With one type of on-line octane analyzer, engine conditions are not disturbed and the engine is operated alternately 4 min on the prototype and 4 min on the product. The knock intensity on the product is compared with the two bracketing prototype knock intensities, and the difference is converted to Δ octane from target.

The standard deviation of a single Δ octane is well below ±0.1 octane. Because a new product sample is tested every 8 min during blending, the repeatability error for the blend is insignificant.

Clearly, the octane target can be lowered when going from batch blending and laboratory octane tests to in-line blending and on-line octane analyzers.

Assuming a ±0.05 octane standard deviation for in-line blending, a ±0.08 range will include 90% of the results.

With a target of 0.08 octane above the specification, there is a 95% chance that the specification will be met. With batch blending, where octane ratings are obtained in a research and a motor octane engine, the target must be set 0.4(R+M)/2 above specification to obtain a 95% chance that the specification will be met. As illustrated by the chart, going from batch blending to in-line blending should allow about a 0.3 octane decrease in the target, resulting in substantial savings.

**Taking full advantage.** In many cases, refiners with in-line blending systems do not take full advantage of the decrease in octane quality giveaway that can be obtained. When in-line blending is first installed, the usual practice is to make blends into tanks and continue certifying the product octane in the tank using laboratory engines (ASTM D2699 and D2700).

This practice is understandable because the refiner must obtain experience with, and confidence in, the on-line octane analyzers. However, in some cases the practice is continued indefinitely. The advantage of on-line octane analyzers is lost. The use of laboratory engines to check on-line octane analyzers has been appropriately called "checking a micrometer with a ruler."

Current octane analyzers are combined with a computer so that the effects of tank heels on octane can be taken into account. The computer can also be used to record Rvp and other volatility data.

Deviation from target octane and volatility can be used in manual or automatic control of qualities. The blend can be held very close to the target, and the computer can report the cumulative deviation from target so that corrections can be made to put the total blend right on target.

With in-line blending and on-line analyses, most refiners are certifying quality on the basis of the on-line analyses.

In many cases, the gasoline is going directly into pipelines and tankers without intermediate storage. In a few cases, the information provided by the on-line analyzers is used in linear programming to reoptimize and change gasoline composition "on the fly" while continuing to meet all specifications.

Much experience has been gained using in-line blending of gasolines and on-line analyzers. Equipment and procedures have been improved. Economic advantages of using in-line blending and on-line analyzers are considerable.

Refiners who are practicing in-line blending should review their procedures to make sure they are making full use of the advantages. Refiners who are not using in-line blending should take a realistic look at their quality variation, then reevaluate in-line blending. ▪

TECHNOLOGY

# Lube facility makes high-quality lube oil from low-quality feed

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A new lube-oil complex that makes premium lubes from crude oils that are deficient in high-viscosity-index ~~(VI)~~ components was started up at Chevron's Richmond, Calif., refinery in late 1984. The project features a large hydrocracking complex with a design production capacity of 9,000 b/d.

Waxy hydrocracked distillates are catalytically dewaxed for the first time ever, producing high-quality lubes from feedstocks which are uneconomical for lubes by conventional processing.

Design features of the complex enable Chevron to achieve the upgrade with low operating costs. The complex is based on Chevron technology developed during the past 10 years.

Historically, Chevron has been a large buyer of high-VI lube base oils. Purchases grew to as much as 6,000 b/cd after the shutdown of an aging Duosol plant in 1981.

That shutdown left the Unocal refinery in Rodeo, Calif., as the only high-VI lube plant on the U.S. West Coast. West Coast demand has been met through large movements of base oils from the Gulf Coast and foreign purchases.

Chevron conceived the Richmond lube oil project (RLOP) in 1978 to eliminate its dependence on other base-oil suppliers. The major objective of RLOP was to produce premium-quality lubes from readily available crudes used for prime fuels production.

**Feed flexibility.** Conventional lube plants use solvent extraction to improve the VI of lube base oils. Solvents like n-methyl-2-pyrrolidone (NMP), furfural, or the older Duosol are used to extract low-VI components (especially multi-ring aromatics), leaving a raffinate of high-VI components (like branched paraffins and single ring naphthenes or aromatics).

But lube plants based on solvent extraction have only limited feed flexibility. High-VI components are merely separated—they cannot be created in the extraction process.

Medium-quality feeds containing relatively few high-VI components require very high solvent-to-oil ratios. Low-quality feeds may not contain any appreciable amount of high-VI components, and can't make high-VI lubes, regardless of solvent dosage.

Richmond's old Duosol lube plant required a select, high-quality feed in order to meet its high-VI product target. In the past, good lube crudes were generally available, but in the last few years before its shutdown, the Duosol plant required expensive Arabian Light resid, shipped from Chevron's Pascagoula, Miss., refinery.

That movement was costly and limited the flexibility of both refineries. This burden was expected to grow as high-quality feeds declined and as lubricant evolution demanded even higher-quality base oils.

Hydrocracking is the best answer to feed flexibility requirements. It is not limited by the mere separation of good components from bad—it creates high-VI components.

Table 1

## Properties of some heavy vacuum gas oils

| Crude | Gravity, °API | Sulfur, wt % | Nitrogen, ppm | Wax, liq vol % | Waxy VI | Dewaxed VI |
|---|---|---|---|---|---|---|
| Sumatran Light | 29.9 | 0.1 | 680 | 54.5 | 132 | 67 |
| Arabian Light | 20.1 | 2.8 | 1000 | 16.7 | 72 | 50 |
| Kuwait | 19.3 | 3.1 | 960 | 7.4 | 66 | 50 |
| Sumatran Heavy* | 21.4 | 0.2 | 1750 | 11.7 | 57 | 36 |
| Alaskan North Slope* | 18.4 | 1.4 | 2420 | 7.0 | 30 | 15 |
| California Light§ | 17.7 | 1.0 | 6200 | 7.6 | 33 | 5 |
| California Heavy† | 11.4 | 1.2 | 7400 | 0.1 | −200 | −228 |

* These crudes are not economic sources of high-VI lubes using conventional solvent refining.

† This crude is not an economic source of high-VI lubes even using hydrocracking technology.

§ This is a blend of light California crudes including 77% of Elk Hills Stevens.

With hydrocracking, "nonlube crudes," like Alaskan North Slope (ANS) and certain California crudes, become viable candidates for high-VI lube production. The greater availability and generally lower cost of these lower-quality crudes enhance the profitability of lubes.

Table 1 shows the feed quality of several different crudes as represented by the VI of dewaxed, heavy vacuum gas oil. Conventional solvent extraction is generally uneconomic for any feed under about 50 VI.

Hydrocracking extends the range of economic feed VI to 0 or even lower. The RLOP currently feeds ANS crude because of its abundance. However, RLOP has fed better (Sumatran Light crude) and worse (a California crude blend called waxy light heavy).

**VI droop.** Besides its lower VI compared to a typical lube crude like Arabian Light, ANS creates another significant challenge in lube hydrocracking—its cracked products exhibit a dramatic variation in VI over the lube-oil boiling range.

Table 2 illustrates this variation for a case geared to production of 100 VI, heavy neutral (500 SUS at 100° F.).

The medium neutral (240 SUS at 100° F.) comes out at only 92 VI, and the light neutral (100 SUS at 100° F.) at less than 80 VI. For comparison, Table 2 also shows an Arabian Light VI profile of 100, 99, and 88 for the same viscosity neutrals.

There are several feasible schemes to overcome VI droop. First, the low-VI front end could be downgraded to fluid catalytic cracker feed, but the yield penalty would be severe.

Second, the severity of the hydrocracker could be increased to raise the overall VI level (giving away VI on the heavy lubes), but again the yield penalty would be substantial.

Third, the light lubes could be recycled to the reactor at the expense of higher investment and operating costs.

The best solution may be to operate the hydrocracker in blocks, feeding heavy distillates to make heavy lubes and feeding light distillates to make light lubes. However, block operation entails extra tankage, greater operating complexity, and higher operating costs.

The RLOP solution to VI droop was to build two hydrocrackers. The first produces all the heavy and much of the medium neutral from heavy distillates. The second produces the balance of the medium and all of the light neutral from lighter distillates.

VI giveaway is minimized by controlling the first to the heavy neutral requirement and the second to the light-neutral requirement. Medium-neutral VI is adjusted by varying the blend ratio of medium neutrals from the two crackers.

Building two hydrocrackers gave Chevron advantages similar to blocked operation. There are two blocks operated continuously and simultaneously in parallel hydrocrackers.

Having two crackers increased the project cost somewhat but avoided the complicated refinery coordination and product downgrading which would have accompanied block switches on one of the refinery's major conversion units. The extra expense of two smaller crackers compared to a single larger one was offset somewhat by eliminating the requirement for feed tankage.

Feeds come hot, directly to the crackers from crude distillation, avoiding the capital and operating costs associated with cooling and reheating the feed. Continuous production of the same products also makes it far easier to keep both lubes and fuels byproducts on test at a consistently higher quality.

**Process flow.** Fig. 1 is a schematic flow diagram of the RLOP project. The project takes advantage of existing units wherever possible.

Raw distillates are cut in an existing large crude unit. Supplemental feed for the heavy cracker comes from a new vacuum column added to an existing deasphalted oil (DAO) hydrocracker.

The heavy hydrocracker produces waxy precursors for both heavy and medium neutrals, in addition to a full spectrum of high-quality byproducts from LPG to FCC feed. The light hydrocracker produces waxy precursors for both light and medium neutrals, in addition to high-quality byproducts ranging from LPG to high-cetane diesel.

Tables 3 and 4 show typical yields and product inspections for both crackers.

Waxy, heavy-neutral oil is dewaxed in a debottlenecked solvent-dewaxing unit. The dewaxed oil is furnished in a new, high-pressure, heavy-neutral hydrofinisher. Medium and light neutrals are blocked through a single high-pressure unit for catalytic dewaxing and hydrofinishing. The catalytic dewaxer is the first ever to feed waxy hydrocracked lubes.

The project also included several auxiliary units to support the lube complex:

- A hydrogen recovery unit to recover purified hydrogen from bleed gas and separator offgas streams from both existing and new hydrocrackers
- An incremental makeup hydrogen compression unit
- A gas recovery unit to separate and recover light ends from the new hydrocrackers and the catalytic dewaxer
- Additional reactors, and a new vacuum column in the existing DAO hydrocracker to provide incremental feed for the heavy cracker
- A new sour-water treating plant to produce ammonia for sales from hydrocracker sour water
- A state-of-the-art control center featuring advanced computer control and monitoring capabilities
- State-of-the-art catalytic NOx reduction facilities for all process furnace flue gases
- New storage and shipping facilities

**Product quality.** The RLOP is the first commercial plant to produce high-VI lubes by an all-hydrogen approach—hydrocracking followed by catalytic dewaxing and hydrofinishing. RLOP's base oils are superior to conventionally produced solvent-refined oils in several respects:

- Lighter color (almost water-white)
- Better oxidation performance (up to twice the life of solvent neutrals in the standard turbine oil stability test)
- Better response to pour-point depressants
- Better viscosity-temperature performance (100 VI RLOP 100 neutral has a lower viscosity at freezing temperatures than a 100 VI 100 neutral produced conventionally).

The all-hydrogen approach gives

Table 2

## VI droop in hydrocracking

| | Alaskan North Slope VI | Alaskan North Slope Droop* | Arabian Light VI | Arabian Light Droop* |
|---|---|---|---|---|
| Heavy neutral, 500 | 100 | Base | 100 | Base |
| Medium neutral, 240 | 92 | 8 | 99 | 1 |
| Light neutral, 100 | 75 | 25 | 88 | 12 |

* Droop is the difference between the VI's of a light and heavy lube oil produced simultaneously by hydrocracking.

Table 3

## Typical yields from lube hydrocrackers

| | Light hydro-cracker | Heavy hydro-cracker |
|---|---|---|
| $H_2$ consumption, scf/bbl | 1,100 | 1,050 |
| **Yields, LV %** | | |
| LPG | 2.6 | 2.3 |
| Gasoline | 12.7 | 7.5 |
| Jet fuel | 33.9 | 20.9 |
| Diesel | 22.3 | 16.3 |
| FCC feed | — | 17.6 |
| Waxy 100 neutral | 23.0 | — |
| Waxy 240 neutral | 18.0 | 29.6 |
| Waxy 500 neutral | — | 15.6 |
| **Total** | **112.5** | **109.8** |
| Controlling product | 100N | 240N |
| Dewaxed oil VI | 103 | 101 |

base oils containing only trace amounts of sulfur, nitrogen, and polycyclic compounds. Aromatic carbon as measured by refractive index-density-molecular weight (n-d-M) analysis is nil.

Table 5 shows base-oil specifications and typical inspections of RLOP products from the first year of commercial production. Typical inspections of solvent neutrals are also included in Table 5 for comparison.

**Complex integration.** The new lube units are tightly integrated to minimize operating costs. For example, distillates from the crude unit are routed directly to the crackers at about 425° F.

Using hot feed reduces the fuel requirements and increases the steam generation in the crackers. Of course, the heat economy doesn't come free.

The direct feed means that the crackers are very sensitive to changes in the crude unit, particularly during crude rate or operating mode changes. Distillation changes that would be of little consequence to a downstream cat cracker can cause major changes in the bottom rate of the vacuum column at the lube cracker. The best example of integration is the combined catalytic dewaxer and hydrofinisher for the light and medium neutrals. This plant uses a single, high-pressure loop with two close-coupled reactors.

The first reactor contains the dewaxing catalyst. The second contains the hydrofinishing catalyst. This arrangement not only avoids an extra cooling and heating step, but it literally avoids all of the investment and operating costs of a separate high-pressure plant, except for the cost of the additional reactor.

A dedicated, closed-loop, tempered-water system is used to integrate low-level cooling and heating requirements throughout the complex. This system was originally conceived only to cool the waxy lube streams while avoiding the freezing problems associated with conventional cooling-tower water, and the mechanical problems associated with recirculating tempered-air fin coolers. But the system soon grew as the hot water was seen to be an acceptable replacement for steam heating in several applications. The hot water is now used as the sole heat supply to reboilers in the gas recovery unit's depropanizer, and the sour-water unit's ammonia rectifier, as well as preheat for combustion air in all the process furnaces.

To provide flexibility for individual plants being out of service, the air fin coolers contemplated for top circulating reflux on all of the vacuum columns were changed to tempered-water heaters during the process design.

Another example of integration is the use of single steam-generation kettles to recover heat from several different services. The lube complex has many small streams that require cooling to rundown temperatures. In the past, these streams would not have ever been considered as steam generation candidates because the recoverable heat would not be able to pay out the necessary equipment. By arranging them as several tube bundles poking into the same kettle, the equipment cost was reduced enough to justify the incremental heat recovery.

A final example of integration is the use of common catalytic denox ($NO_x$ removal) systems for several process furnaces. The requirements of the local air pollution control agency dictated catalytic denox systems in addition to staged-fuel, low-$NO_x$ burners.

To avoid the cost and complexity of separate denox systems for each of the 10 process furnaces in the project, the furnaces were arranged into three "clusters" of three or four furnaces each. Each cluster is served by a single catalytic denox system consisting of a forced draft fan, 450 psig steam generation section, chemical injection system, catalyst bed, economizer section, induced-draft fan, stack, and all associated instrumentation and controls.

**Reduced operating costs.** As shown by the integration examples above, the RLOP was specifically designed to minimize operating costs. In any hydroprocessing application, hydrogen is the major operating cost, and the RLOP is no exception.

To minimize the cost of hydrogen generation, an elaborate hydrogen recovery system was built to reclaim the hydrogen content of bleed streams and separator offgases from all the hydrogen-consuming plants. Low-pressure separators in the consuming plants are designed to operate at 500 psig to allow dissolved hydrogen to be included in the recovery system without any additional compression.

High-pressure recycle compressor seal-trap offgases are also vented to the recovery system. The collected gases are treated to remove ammonia and $H_2S$, cooled to condense heavy hydrocarbons, and purified in a pressure swing adsorption system (PSA).

The PSA unit contains multiple adsorbents to retain light hydrocarbons and nitrogen and allow pure hydrogen to pass through at pressure. The adsorbents are regenerated by reducing the pressure to desorb the impurities. The released impurities are then compressed to the refinery fuel system pressure.

A major operating cost in any solvent dewaxing plant is the energy needed to provide refrigeration of the waxy oil-solvent mix. In a conventional plant, refrigeration compressors (using propane, propylene, or ammonia refrigerants) are typically driven by high-cost, high-pressure steam. At RLOP, the solvent dewaxer for heavy neutral uses an entirely different type of refrigeration—aqua ammonia absorption refrigeration (AAAR).

In an AAAR system, pure anhydrous liquid ammonia is vaporized in the chiller at a low pressure, controlled to give the desired refrigerant temperature, just as in a conventional compression-refrigeration loop. But instead of compressing the low-pressure ammonia, AAAR works by absorbing it with a dilute aqua-ammonia solution to form a rich aqua-ammonia stream. The rich liquor is pumped up to a rectifying column operating at about 200 psig. The rectifying column

Table 4

## Typical component properties from lube hydrocrackers

| | Light hydro-cracker | Heavy hydro-cracker |
|---|---|---|
| **Gasoline** | | |
| API gravity | 64.0 | 63.5 |
| **Jet fuel** | | |
| Gravity, °API | 40.0 | 38.2 |
| Flash point, °F. | 110 | 110 |
| Freeze point, °F. | -65 | -65 |
| Smoke point, mm | 21 | 20 |
| **Diesel** | | |
| Gravity, °API | 33.4 | 30.6 |
| Pour point, °F. | -10 | -10 |
| Cetane index | 52 | 47 |
| **FCC feed** | | |
| Gravity, °API | — | 30.4 |
| Sulfur, ppm | — | <1.0 |
| Nitrogen, ppm | — | <0.2 |

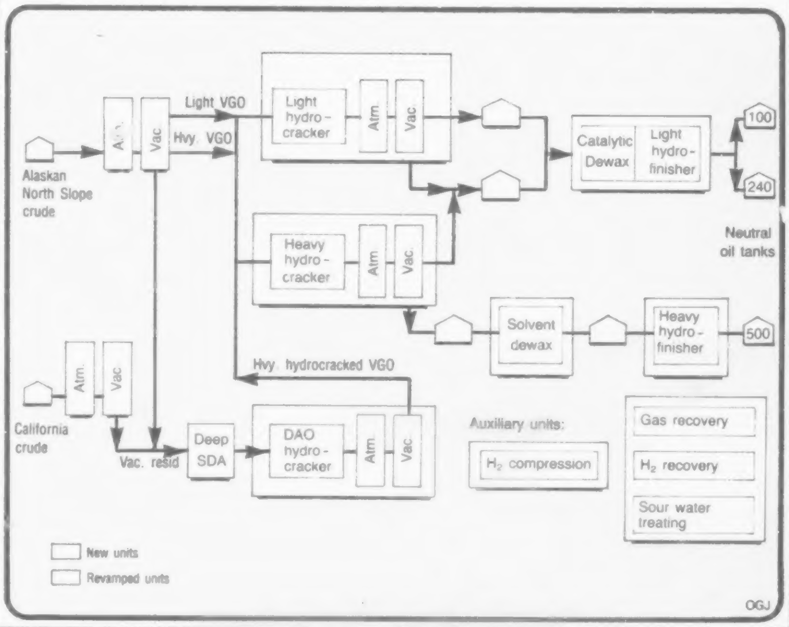
Table 5

## Neutral oil quality

| | RLOP specification | RLOP typical | Solvent typical |
|---|---|---|---|
| **100 neutral** | | | |
| Viscosity, cSt @ 40° C. | 18.8 - 20.9 | 19.31 | 18.88 |
| Viscosity, cSt @ 100° C. | — | 3.97 | 3.88 |
| Viscosity index | 95 min. | 99 | 95 |
| Color, ASTM D 1500 | 1.0 max. | L 0.5 | 1.0 |
| Pour point, °F. | 15 max. | 10 | 10 |
| Flash point, °F. | 380 min. | 395 | 380 |
| **240 neutral** | | | |
| Viscosity, cSt @ 40° C. | 44.0 - 48.0 | 46.70 | 46.50 |
| Viscosity, cSt @ 100° C. | — | 6.80 | 6.68 |
| Viscosity index | 95 min. | 99 | 95 |
| Color, ASTM D 1500 | 1.5 max. | L 0.5 | 1.5 |
| Pour point, °F. | 15 max. | 10 | 10 |
| Flash point, °F. | 435 min. | 450 | 415 |
| **500 neutral** | | | |
| Viscosity, cSt @ 40° C. | — | 95.20 | 95.90 |
| Viscosity, cSt @ 100° C. | 10.7 - 11.4 | 11.11 | 10.75 |
| Viscosity index | 95 min. | 101 | 95 |
| Color, ASTM D 1500 | 2.5 max. | 0.5 | 2.5 |
| Pour point, °F. | 15 max. | 10 | 10 |
| Flash point, °F. | 475 min. | 500 | 450 |

Fig. 1

## RLOP project flow diagram


Light VGO
Hvy. VGO
Atm.
Vac
Alaskan North Slope crude
Light hydro-cracker
Atm
Vac
Catalytic Dewax
Light hydro-finisher
100
240
Neutral oil tanks
Heavy hydro-cracker
Atm
Vac
Solvent dewax
Heavy hydro-finisher
500
Hvy. hydrocracked VGO
Atm.
Vac
California crude
Vac. resid
Deep SDA
DAO hydro-cracker
Atm
Vac
Auxiliary units:
$H_2$ compression
Gas recovery
$H_2$ recovery
Sour water treating
New units
Revamped units
OGJ

19-FA-1

produces an anhydrous liquid ammonia overhead stream and a dilute aqua-ammonia bottoms to complete the loop. The reboiler heat requirement for the rectifier is satisfied by low-cost 15 psig steam which is often vented in many refineries.

Operating costs of the hydrocrackers are minimized by use of a scheme which exchanges heat between reactor, atmospheric, and vacuum distillation sections. Temperature approaches were squeezed to maximize heat recovery and minimize duty requirements for process furnace. Recycle compressors are driven by turbines which take advantage of excess, low-cost, low-pressure steam.

**Operating experience.** Any large, new process plant complex presents a significant startup challenge. Recruiting and training operators, establishing coordination with an existing refinery infrastructure, and break-in of new process equipment are difficulties common to all major projects.

Lube projects are further complicated by rigorous and often unfamiliar product quality considerations, and by the sequential arrangement of the process steps. Each process step may directly control only one or two of the final product specifications, but may indirectly affect several others.

For example, the catalytic dewaxer sets the pour point, but also causes significant changes to VI and viscosity. Larger-than-expected shifts in VI would require corresponding changes in the upstream hydrocracker.

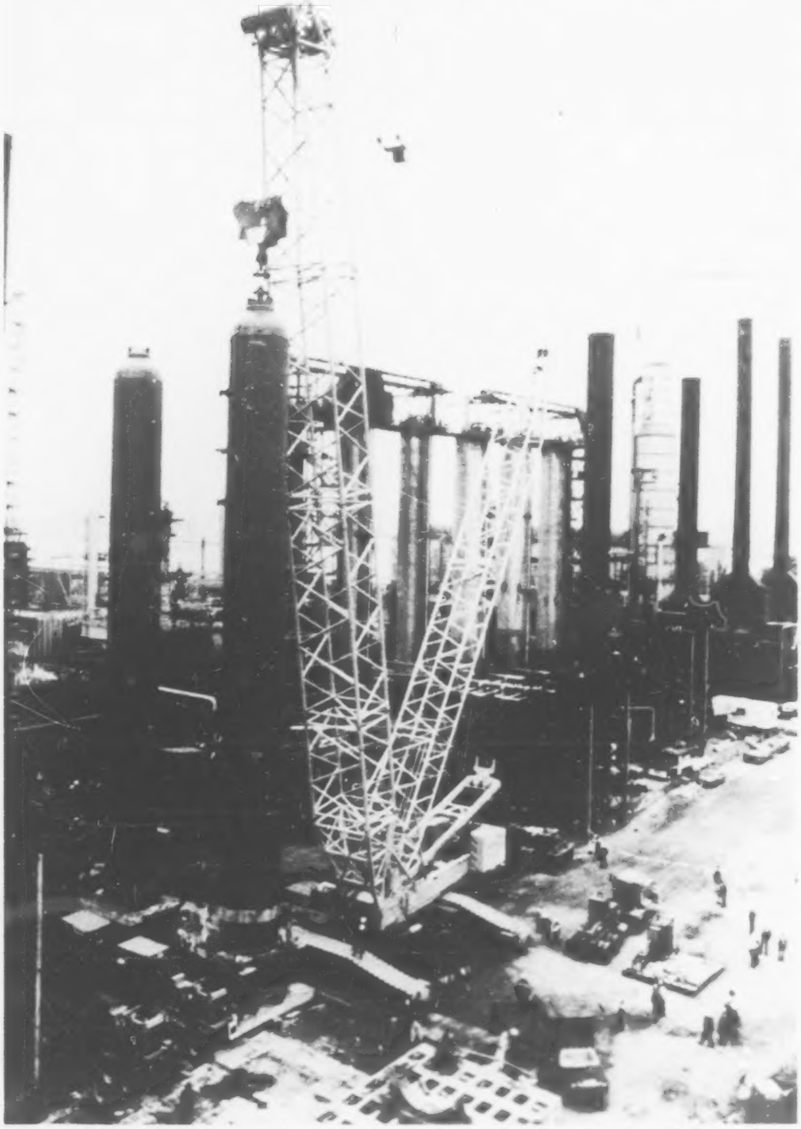
The RLOP project was complicated still further by two additional factors: the tight systems integration mentioned earlier for reducing operating costs to the minimum, and the novelty of the process. In addition to having Chevron's first commercial lube hydrocracker, the RLOP features the world's first use of catalytic dewaxing in conjunction with hydrocracking.

Two brand new catalysts were developed from concept through commercial production for this project.

The startup period lasted about 6 months, from starting the first hydrocracker through sustained operation of the last hydrofinisher. The heavy hydrocracker was the first to see feed in August 1984.

Startups of the light hydrocracker and light hydrofinisher were plagued by serious subsynchronous vibrations in the high-pressure feed pumps. A major joint redesign effort between Chevron and the pump manufacturer was needed to solve the problem.

It wasn't until late 1984 that the light cracker was able to run. A shortage of hydrogen due to an unscheduled hydrogen plant shutdown further restricted lube production. Finally, in January 1985, all the plants were up and running, and full attention was focused on increasing lube produc-



**New reactors added** to Chevron's RLOP project. Existing reactors of Isomax plant are shown behind the crane.

## The authors...

**Farrell**

**Zakarian**

Thomas R. Farrell is a senior engineering associate in the process design division of the process engineering department at Chevron Research Co. He is responsible for process engineering support for Chevron and licensee lube plants.

Farrell has been involved in many areas of petroleum processing technology, concentrating on correlation, design, start up, and troubleshooting of various hydroprocessing units for the past 9 years. He led the process design teams for the two RLOP hydrocrackers and he was in charge of all process aspects of the start-up of the process at the refinery. Farrell has a BS in chemical engineering from the University of Wisconsin.

Jack A. Zakarian is a senior research engineer in the lube processing section of the hydroprocessing division in the process research department of Chevron Research Co. He is responsible for continuing lube process development, including hydrocracking, catalytic dewaxing, hydrofinishing, and solvent extraction.

Zakarian was a major contributor to the process and catalyst development of Chevron's lube hydroprocessing technology, and he provided process engineering, start up, and operational support for the RLOP project. He has BS degrees in chemistry and mathematics from Massachusetts Institute of Technology, an MS in chemistry, and MS and PhD degrees in chemical engineering from the University of California at Berkeley.

tion.

Finished lube production averaged only about half of design in early January. As operating skill increased and process adjustments were made, the production rate began a steady climb, reaching design capacity by late February 1985. The production performance of the lube complex is a tribute to the skills of the RLOP's operators and operating supervisors.

**Dewaxing comparison.** Chevron's initial interest in catalytic dewaxing was spurred by a desire for reduced operating and capital costs compared to solvent dewaxing. In catalytic dewaxing, a shape-selective hydrocracking catalyst is used to selectively crack the waxy molecules (mostly normal paraffins), leaving the wax-free molecules mostly untouched. The cracked wax is converted primarily to propane, butane, and light gasoline, which are easily separated from the uncracked lube oil in a product stripper.

With a "perfect" dewaxing catalyst, only the wax is cracked, so the yield of lube oil would be equivalent to solvent dewaxing (or somewhat better, considering the oil retained in slack wax). Actual yields are somewhat less than for solvent dewaxing, indicating that the catalyst is not perfectly selective for wax.

Catalytic dewaxing to a 10° F. pour point also results in a loss of several VI numbers and a kinematic viscosity increase of about 10-15% compared to solvent dewaxing, suggesting that the catalyst also cracks away some high-VI, low-viscosity molecules.

The expected cost savings for catalytic dewaxing have, in fact, been realized commercially, especially when the dewaxer is integrated with the hydrofinisher as at the RLOP. Somewhat offsetting the lower costs of dewaxing is the increased severity needed in the hydrocrackers to overcome the VI loss of catalytic dewaxing.

**Licensing.** The 1984 Chevron/Gulf merger united the two major licensors of lube hydrocracking technology. The RLOP units boost the total capacity of Chevron/Gulf-licensed lube hydrocrackers to 80,000 b/d—more than 80% of the world's capacity. ▪

# Distillation sequence with fixed degree of

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Although methods exist for the optimal design of distillation sequences, no current method systematically takes flexibility into account. Flexibility and uncertainty are traditionally examined in the context of process control rather than process design.

A simple method has been developed which optimally designs a distillation sequence with a fixed degree of flexibility in feed composition and flowrate. This method minimizes the estimated annual venture cost and assures both optimal and feasible operation in a range of flexibility/uncertainty by using an approach termed "practical feasibility."

Under certain changing conditions, the optimal separation sequence may not be the same as the one that was determined when nominal conditions were used in the design.

Distillation is the single most widely used separation method in the chemical industry today. Its relative simplicity, combined with its wide applicability, make it very attractive as a separation process.

However, distillation is highly energy intensive. Because of this, many attempts have been made to reduce the energy consumption and optimize the distillation sequence.

Optimization methods have included resequencing of the distillation network, heat integration between columns, vapor recompression, and the use of complex towers, i.e., more than two product streams. In each of these methods, the main thrust is to reduce the total cost of the distillation, capital plus operating. Because energy costs are so high, the potential savings are significant, i.e., 3-10% for optimal sequence compared to a standard sequence.

Of these methods, those involving resequencing and heat integration have received the most attention. They have dealt with determining the best sequence under specified nominal process conditions. However, other factors related to the operability of the plant, such as flexibility, controllability, reliability, and safety, also need to be accounted for at the design stage.

Flexibility is the ability of a process to operate feasibly and optimally in the presence of varying or uncertain conditions.

For distillation, there are two types of uncertain parameters. Operational parameters may include product specifications, inlet temperatures, pressures, flowrates, or compositions. They reflect changes due to plant upsets, changing market conditions, or differing feedstocks.

Technological parameters may also be uncertain, such as heat transfer coefficients and column efficiencies. These variations represent uncertainties in the parameters used in the mathematical models of the process. They occur because there is a lack of good models or experimental data in the particular region of interest.

The operational parameter uncertainties may represent the flexibility desired in the process. The technological uncertainties need to be protected against, lest they cause the process to operate infeasibly, i.e., not meeting specifications.

Traditionally, flexibility has been incorporated in a process on the basis of an engineer's experience and judgment. Usually this was done by designing the distillation sequence at the nominal, most likely, values and then applying some empirical overdesign factor. Clearly this type of solution doesn't give much insight into the degree of flexibility in the design. The amount of overdesign may be very difficult to justify on economic grounds.

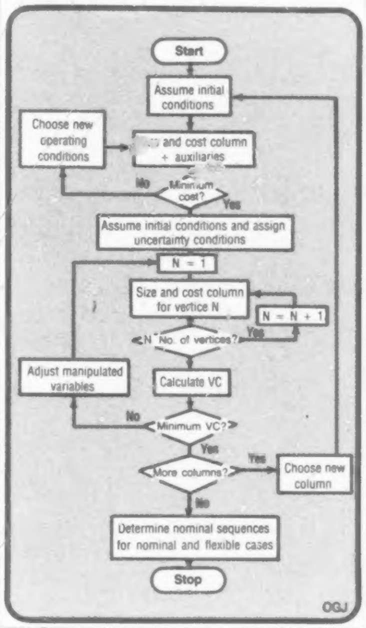
Although there have been several approaches to incorporate flexibility into chemical plant designs, none have been solved explicitly for distillation columns with or without heat integration. Also, only a few have tried to take into account uncertainty, and only one has dealt with the concept of flexibility.

The main drawback of previous approaches has been the lack of consideration of guaranteeing feasible operation over an entire uncertain parameter space. One approach (Halemane and Grossman 1982, 1983) guaranteed such feasibility.

They showed that for convex constraint functions there exists a critical vertex on the uncertain parameter space which guarantees feasibility over the entire space, if this vertex is feasible.

Fig. 1

Flexible sequence


Start
Assume initial conditions
Choose new operating conditions
and cost column + auxiliaries
No
Minimum cost?
Yes
Assume initial conditions and assign uncertainty conditions
N = 1
Size and cost column for vertice N
N = N + 1
N ¯ No. of vertices?
Yes
Adjust manipulated variables
Calculate VC
No
Minimum VC?
Yes
More columns?
Yes
Choose new column
No
Determine nominal sequences for nominal and flexible cases
Stop
OGJ

The drawback of this method is the possible large number of vertices and the difficulty in determining the critical one. However, an efficient algorithm was developed for checking all the vertices and thus guaranteeing feasibility.

**Solution method.** The correct design of an optimal, flexible distillation column can be expressed as, "that design which will operate feasibly at any value of the uncertain/flexible parameters, and which minimizes the expected venture cost (VC) of the distillation column." Mathematically, it is a two-stage minimization problem: One solution represents an outer optimization problem which includes the feasibility constraints. The inner optimization ensures optimal operation for a given set of fixed design variables and uncertain parameters.

Traditionally, the inner solution has been used as the basis for optimal design of distillation columns and sequences. When uncertainty/flexibility has been taken into account in the design of distillation columns, investi-

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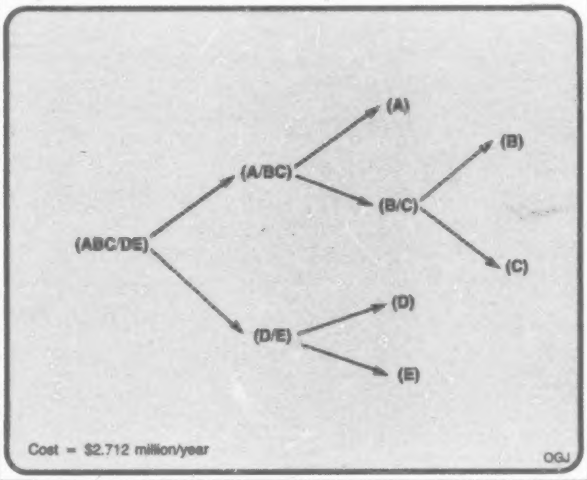
From a presentation made at the 6th Large Chemical Plants Conference, Antwerp, Belgium, Oct. 9-11, 1985. Complete proceedings are available from Technologishch Instituut-K.VIV, Jan Van Rijswijcklaan 58, 2018 Antwerpen, Belgium, at a cost of 2000 BF.

# flexibility can handle feed changes

Fig. 2

Optimal nominal sequence



Cost = $2.712 million/year

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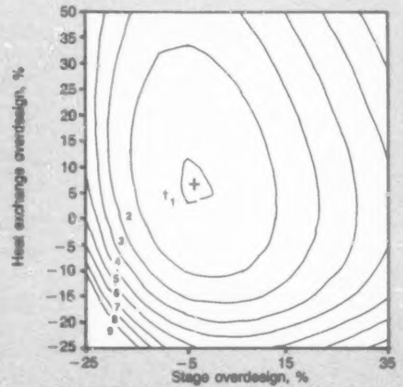
Fig. 3

Case 1 venture cost variations*



*Optimal venture cost, $2,592,739/year. Uncertainty ±25% for all components. I = 0.25, 0.25, 0.25 (high, low, nominal). †Legend: cost areas, $/year 1−2,595,00 2−2,925,000 3−2,955,000 4−2,985,000 5−3,015,000 6−3,045,000 7−3,075,000 8−3,105,000 9−3,135,000

OGJ

gators have used optimization solution without including feasibility constraints. This occurred because of the computational difficulty in including these constraints, and the fact that an entire uncertain parameter space must be searched.

As a result, an attempt has been made to narrow the search space so that if feasibility is maintained for a finite number of vertices in the uncertain space, then feasibility could be guaranteed over the entire uncertain /flexible parameter space.

Practical feasibility describes an approach to determine the critical vertices or those combinations of uncertain/flexible parameters which guarantee feasibility over the entire uncertain/flexible space if feasibility is ensured for these vertices. This is accomplished by considering the general knowledge and operating characteristics of the distillation column.

The first step is to determine the constraints which need to be met over the uncertain/flexible parameter space. This is followed by a detailed examination of these constraints.

For a distillation column, the operating constraints are:

- Maintain product purity.
- Ensure feasible operation of the reboiler and condenser.
- Ensure that the column is not in a flooding condition.
- Ensure that the column is not in a weeping condition.

These constraints must be put into mathematical statements and examined so that the critical vertices can be determined.

The first constraint, maintain product purity, is an equality constraint. Any value less than the desired value implies infeasible operation. Product purities greater than the specified amount give no bonus, i.e., greater product selling price.

For this work, the product purity was specified as 98% recovery of the light and heavy key components. It is necessary to guarantee that this required recovery is possible no matter what the feed composition. This is easily accomplished by ensuring that the column has more stages than the lowest minimum number which occurs in the uncertain parameter space.

Minimum stage requirements are independent of the feed composition and depend only on the separation requirements. Thus the minimum number of stages remains constant for constant pressure operation since the separation requirements are constant.

Therefore, product purity is guaranteed, and the first constraint will be met over the uncertain parameter space, if the stage requirements are met for any feed composition within the uncertain space.

The second constraint can also be viewed from the concept of practical feasibility. For heat exchangers, feasible operation implies that regardless of the heating or cooling duty required, the heat exchanger can transfer that amount of energy using the available utilities.

The governing equation for heat exchanger operation is:

$$Q = UA\Delta T$$

where:

$Q$ = Rate of energy transfer, BTU/hr

$U$ = Overall heat transfer coefficient, BTU/hr sq ft °F.

$\Delta T$ = Log mean temperature difference

$A$ = Heat exchanger area

Once the area of the exchanger is fixed, the required heat transfer is accomplished by varying the temperature of the utilities. Steam is used as the utility in the reboiler, while cooling water or refrigerants are used in the condenser, depending on the temperature requirement.

The exchanger is designed for the largest heat duty, with an assumed overall heat transfer coefficient of 100 BTU/hr sq ft °F. The utilities temperature is then calculated based on the required temperature difference. For different heat duties, the log mean temperature difference (LMTD) is calculated based on the changes in overall heat transfer coefficient and duty, and solving the equation along with the heat balance equation for each stream.

Since it is assumed that the steam and refrigerants are available at any temperature, it is simply a matter of

Table 1

## Test data

| Index | Component | Mole fraction | Relative* volatility |
|---|---|---|---|
| A | Propane | 0.05 | |
| B | i-butane | 0.15 | 2.971 |
| C | n-butane | 0.25 | 1.503 |
| D | i-pentne | 0.20 | 2.925 |
| E | n-pentane | 0.35 | 1.402 |

*Values of the relative volatilities of adjacent components (Ki/Ki + 1) were calculated at 14.7 psia

Table 2

## Case 1 requirements*

| Description | Optimal overdesign, (std. dev.)† Stages | Reboiler | Condenser |
|---|---|---|---|
| Optimal sequence | −3.165<br>(0.5888) | 9.33<br>(2.652) | 4.748<br>(0.6155) |
| All possible columns | −2.93<br>(2.000) | 9.169<br>(2.762) | 5.257<br>(1.199) |

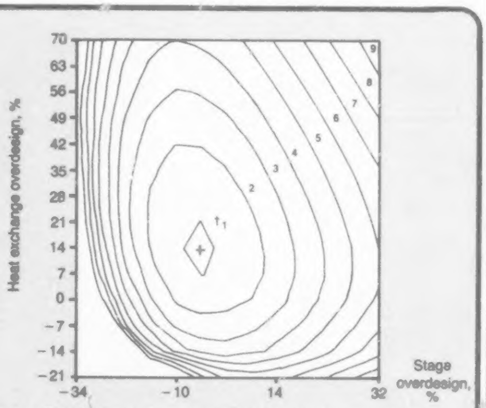
*Uncertainty = ±25% for all components

$\omega_i$ = 0.25, 0.25, 0.50 (high, low, nominal)

† Standard deviations are given in parenthesis.

Fig. 4

## Case 2 venture cost variations*

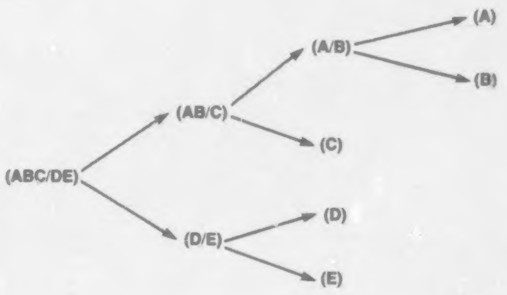


*Optimal venture cost, $3,033,267/year. Uncertainty +50%, −25% for all components. i = 0.125, 0.25, 0.625 (high, low, nominal). †Legend: cost areas, $/year 1−3,036,00 2−3,068,000 3−3,093,000 4−3,128,000 5−3,158,000 6−3,168,000 7−3,215,000 8−3,248,000 9−3,278,000

OGJ

Fig. 5

## New sequence*



*Due to flexibility. Cost = $2.976 million/year = 9.73%.

OGJ

changing the temperature of these utilities to give the required temperature difference. For cooling water, the procedure is slightly different since it is assumed to be available only at 75° F., thus fixing the temperature difference at one end of the heat exchanger.

By ensuring that this temperature difference is greater than or equal to the required LMTD of the exchanger, the flowrate of cooling water can be adjusted so that the outlet temperature difference gives the required LMTD. Thus the feasibility of both the reboiler and condenser can be guaranteed over the uncertain/flexible range.

The third and fourth constraints require feasible operation of the column in hydrodynamic terms. They also can be viewed from the practical feasibility aspect.

Since flooding occurs at the highest vapor flow rate, the set of parameters which gives the highest vapor flow will be the critical vertex for this constraint. The critical vertex for the weeping constraint will be the set of parameters which give the lowest vapor flow, since this is when weeping is most likely to occur.

Thus, if flooding and weeping constraints were explicitly included in the optimization, it would only be necessary to guarantee that these constraints were met at the highest and lowest vapor flows.

However, for sieve trays, the turndown ratio or the ratio of maximum allowable vapor velocity (flooding) to minimum allowable vapor velocity (weeping) is approximately 3. Also, correlations have been given which predict the flooding conditions and thus the minimum diameter which can be used without flooding occurring.

In this work, a correlation given by Heaven (1969) is used to estimate the maximum allowable vapor velocity. Thus, if the column is sized using this correlation for the highest expected vapor flow, the weeping constraint will automatically be met if the ratio of highest to lowest expected vapor flows is less than 3. If there is a situation where this ratio is greater than 3, it would be necessary to include these constraints explicity in the optimization.

Practical feasibility is a useful approach to simplify the constraints needed to guarantee feasibility of operation of a distillation column and its associated auxiliary equipment. These simplifications can be incorporated into an algorithm for the design of optimal flexible distillation columns without heat integration.

**Proposed algorithm.** An algorithm for the design of flexible distillation sequences (Fig. 1) can be summarized as:

- Determine optimal pressures, log mean temperature differences, and reflux ratios for the nominal flow rates and compositions.
- Using the optimal nominal pressure, determine the optimal number of stages and heat exchanger areas for each column taking into account the uncertainty/flexibility requirements.
- Combine the columns to form sequences and determine the cheapest sequence using dynamic programming.

The first step is the traditional optimization of single columns at the nominal (most likely) conditions. In the past, the solution to this problem was used to synthesize the optimal distillation sequence.

However, previous work assumed the temperature difference in the condenser and reboiler by specifying the minimum approach temperature. This assumption has been shown to give unreliable results since the optimal temperature differences may be differ-

Table 3

## Case 2 requirements*

| Description | Optimal overdesign, (std. dev.)† Stages | Reboiler | Condenser |
|---|---|---|---|
| Optimal sequence | -4.163<br>(0.8107) | 18.235<br>(3.687) | 12.03<br>(1.505) |
| All possible columns | -3.853<br>(1.829) | 18.709<br>(3.356) | 12.24<br>(2.379) |

*Uncertainty = + 50 %, -25% for all components.

$\omega_i$ = 0.125, 0.25, 0.625 (high, low, nominal)

† Standard deviations are given in parenthesis.

ent from the assumed values.

At present, the optimization used to solve the first step is an implementation of Box's complex algorithm (Box, 1965) found in Kuester and Mize (1973), with modifications according to Guin (1966).

The objective function to be minimized is the annual venture cost (VC) in dollars. Convergence is assumed if the percentage difference between the best and worst functional values is less than 0.01% for five consecutive iterations.

The second step is the portion of the algorithm where the practical feasibility simplifications are used and where the flexible columns are designed. The objective function is a weighted cost function which defines the expected annual venture cost (VC) and is defined as follows:

$$F = \Sigma\omega_i VC_i$$
$$\Sigma\omega_i = 1.0$$

where:

$\omega_i$ = Weighting factor for vertex i

$VC_i$ = Venture cost for vertex i, \$/year

i = Vertex number

n = Number of vertices

These vertices are chosen to guarantee feasibility of operation (critical vertices) while representing the flexibility/uncertainty requirements as well. The formulation of this objective function also has the advantage of representing the multi-period problem as well or the situation where the plant will operate at various levels (i) for specified fractions of time ($\omega_i$). Once the objective function is defined, the task is to find the optimal equipment sizes and operating conditions to minimize the VC.

The individually optimized columns can now be joined to form sequences. Since the flow of material (information) from one column to the next is serial, i.e., no feedback, the theory of dynamic programming can be used to find the optimal sequence. All the sequences are determined and then ranked according to cost.

This method is simple, yet effectively carries out the task of systematically accounting for uncertainty/flexibility during the design of optimal distillation sequences.

**Results obtained.** To test the algorithm, a series of tests was performed. A problem frequently used in the literature (Rathore, 1974) was used so that the nominal results could be checked against published results.

The problem consists of a five-component, light alkane feed mixture. Composition and flowrate are given in Table 1. A schematic of the optimal sequence is shown in Fig. 2, which is keyed to Table 1.

In each case, it is assumed that the recovery of light and heavy keys is 98%, and that feed and product streams are present at their bubble points. Costs of pumping are assumed to be negligible, while costs of the column, trays, reboiler, condenser, and accumulator are determined using equations regressed from Guthrie (1970) and by Tedder (1975), and translated into 1980 dollars. The columns were designed using the Fenske-Underwood-Gilliland approach.

For the flexibility/uncertainty study, various ranges of flexibility/uncertainty were assumed about the nominal flow rate for each component. Various weightings ($\omega_i$) were used for the nominal, highest, and lowest flowrates. The highest flow rate is required in order to guarantee feasibility of the column operation. The nominal and lowest flow rates were included to represent the required range of flexibility/uncertainty. These preliminary studies were undertaken in order to:

- Compare, economically, various overdesign approaches.
- Examine the effect of uncertainty /flexibility on the optimal sequence.

Various runs were made in which both the levels of the uncertainty/flexibility and weightings were varied. These results were then compared in order to evaluate the implication of various overdesign approaches.

The first case had ±25% uncertainty in the flowrates from the nominal case, and weightings of 0.25, 0.25, and 0.50 for the highest, lowest, and nominal flowrates, respectively. Comparison of various results (Table 2) showed that the optimal overdesign for the condenser and reboiler are significantly different when comparing the results both for the optimal sequence and all 20 possible columns.

Surprisingly, the condenser and reboiler are overdesigned less than might be expected since the maximum flowrate is 25% higher than the nominal. The implications of various overdesign strategies can be seen in Fig. 3 which shows that if the reboiler and condenser are oversized by 25%, corresponding to the worst case, the expected venture cost increased by \$22,000. Furthermore, if the stages are overdesigned by 10%, the expected venture cost is further increased by \$30,000.

A second case had uncertainty/flexibility of +50% and −25% from the nominal value for each flowrate, with weightings of 0.125, 0.25, and 0.625 for the highest, lowest, and nominal flowrates, respectively. Again, (Table 3) there is a significant difference in the required overdesign for the condenser and reboiler, both for the optimal sequence and all 20 columns. The level of overdesign is less than might be expected in light of the large uncertainty levels.

Fig. 4 shows the implications of designing for the worst case. If the reboiler and condenser are overdesigned by 50%, and the stages remain at the nominal value, the expected venture cost is increased by \$56,000. A further increase of \$45,000 occurs if the stages are then overdesigned by 15%.

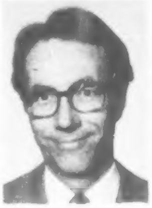
**Effect on optimal sequence.** For the previous results, there was no change in the optimal sequence compared to the nominal case. This is not surprising, since the composition at each of the vertices was the same, and thus one would expect the optimal sequence to be the same for each of these vertices. As a result, other combinations were investigated to determine the effect of uncertainty on the sequence structure.

Generally speaking, the optimal nominal sequence continued to be the cheapest sequence after flexibility/uncertainty had been taken into account. However, an example was found where this was not the case.

The uncertainty conditions for this case and the schematic of the new optimal sequence are shown in Fig. 5. The second best sequence in this new case is the optimal nominal sequence. The difference in VC is only \$5,000/year. However, it still may be said that uncertainty may change the optimal sequence.

Future work will be directed toward

## The authors. . .



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consideration of other uncertainties, such as stage efficiencies, heat transfer coefficients, and economic parameters. Also, a similar method is being developed which will design an optimal flexible heat integrated distillation sequence.

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# Seminole $CO_2$-

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Amerada Hess Corp.'s Seminole (Tex.) San Andres unit $CO_2$-recovery plant incorporates careful design and Ryan/Holmes technology to handle associated gas from a large $CO_2$-flood.

The plant represents one of the first large-scale gas-processing facilities specifically designed to handle associated gas from a $CO_2$-flood project.

Commissioned in late 1984, the plant includes two identical fractionation trains, each of 85 MMscfd design capacity which incorporate Koch Process Systems Inc.'s Ryan/Holmes technology.

**Increased production.** West Texas' Seminole field project is one of the largest $CO_2$-injection projects in the area. At peak rates, more than 200 MMscfd of $CO_2$ are injected into the field. Seminole produced approximately 30,000 b/d of crude oil before injection began more than 2 years ago.

Recent crude-oil production has been more than 35,000 b/d.

Concurrent with oil-production-rate increases, however, $CO_2$ is also produced in increasing quantities with

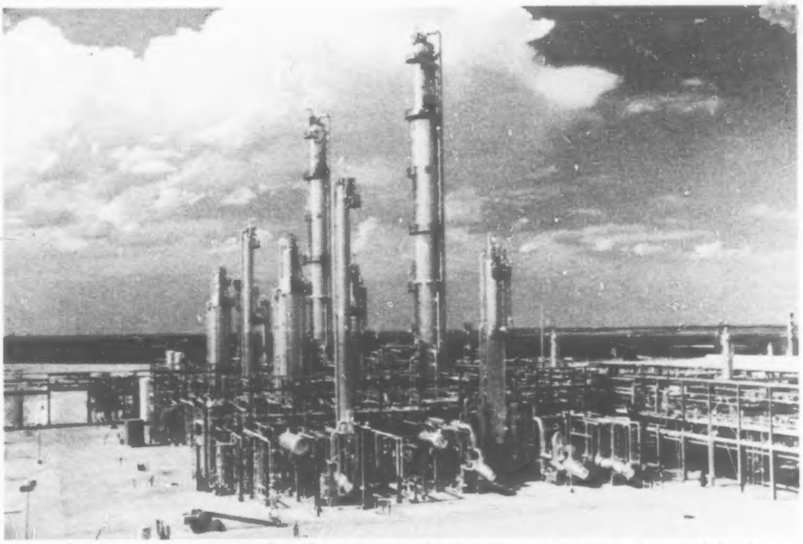
Based on a paper presented to the 65th Annual GPA Convention, Mar. 10-12, San Antonio.

Table 1

### Design feed-gas flow, composition

| | Case A | Case B | Case C |
|---|---|---|---|
| Flow rate, MMscfd | 28.0 | 65.0 | 170.0 |
| Composition, mole % | | | |
| $CO_2$ | 20.9 | 50.0 | 76.9 |
| $H_2S$ | 3.6 | 2.2 | 1.0 |
| $C_1$ | 44.2 | 27.4 | 12.0 |
| Balance | 31.3 | 20.4 | 10.1 |

# flood gas plant has successful early operations



**Amerada Hess Corp.'s Seminole** $CO_2$-recovery plant in West Texas serves one of the largest $CO_2$-flood projects in the area (Fig. 1).

the casinghead gas. This phenomenon presents a serious challenge for the design of the gas plant to be used in conjunction with the EOR flood.

**Design requirements.** The Seminole plant-design basis required that a number of critical separations be made. First of all, $CO_2$ had to be recovered for reinjection into the reservoir, thereby lowering the amount of $CO_2$ required to be purchased over the life of the project.

Methane had to be removed from the recycle $CO_2$ stream to avoid raising the miscibility pressure in the reservoir. Maximum hydrocarbon recovery was to be achieved in order to enhance plant revenues from residue gas and NGL product streams.

In addition, $H_2S$ present in the feed gas was to be removed from both the $CO_2$ and methane streams for safety and sales considerations.

All these demanding separation requirements would challenge any technology, especially when confronted with a rapidly increasing total gas flow and $CO_2$ composition over the project life.

The three feed-gas design cases for the Seminole plant are shown in Table 1. The required product specifications are summarized in Table 2.

**Process technology.** The Ryan/Holmes process utilizes a low-temperature distillative approach to effect the required separations. The process involves three primary separations: $CO_2$-methane; $CO_2$-ethane; and $CO_2$-$H_2S$, all of which employ a circulating NGL additive to provide a particular benefit to the distillation involved.

All the pertinent separations were successfully demonstrated in a pilot plant during 1981. The pilot plant also served to confirm the experimental vapor-liquid equilibrium (VLE) data obtained earlier in the development of the technology (OGJ, Oct. 6, pp. 62-67).

The fact that the technology uses conventional, carbon-steel distillation equipment, modest refrigeration temperature levels, and requires no chemical solvents played an important role in its selection for the Seminole plant application.

The Seminole $CO_2$-recovery plant (Fig. 2) consists of a number of distinct processing units as depicted in the systems diagram (Fig. 3).

These units include process-gas compression, feed-gas dehydration, Ryan/Holmes fractionation (two identical 85 MMscfd trains), $CO_2$ pumping, NGL compression and condensation, NGL treating, and sulfur recovery.

The primary plant utility systems installed to support the process units are as follows: propylene refrigeration system, heat-recovery system on gas-turbine driver exhausts, steam system, and cooling-water system.

Table 2

## Design product specifications

| | | |
|---|---|---|
| Carbon dioxide | | |
| | $N_2$ | 2.0 mole % |
| | $C_1$ | 3.0 mole % |
| | $H_2S$ | 100 ppm vol |
| | $H_2O$ | 4 lb/MMscf |
| Residue gas | | |
| | $CO_2$ | 2.0 mole % |
| | $H_2S$ | 1/4 gr/100 scf |
| NGL (untreated) | | |
| | $C_1$ | 2.0 mole % |
| | $CO_2/H_2S$ | 2/1 |

* Maximum inpurity levels.

Table 3

## Start-up feed-gas conditions

| **Available flow composition** | **27.5 MMscfd mole %** |
|---|---|
| $N_2$ | 1.7 |
| $CO_2$ | 27.3 |
| $H_2S$ | 3.6 |
| $C_1$ | 43.8 |
| $C_2$ | 12.1 |
| $C_3$ | 7.5 |
| $C_4^+$ | 4.0 |

**Dehydration.** Separator gas from the Seminole field is delivered to the $CO_2$-recovery plant at 100 psia. The feed gas is partially dehydrated in a low-pressure triethyleneglycol (TEG) contactor with semi-lean glycol before being compressed to 400 psia in the first section of the process-gas compressor.

Following final dehydration, which takes place at this higher pressure, a coalescer and carbon-bed adsorber ensure complete removal of any glycol carryover. Fig. 5 presents a schematic of the compression and dehydration facilities.

The fractionation section (Fig. 4) consists of a four-column arrangement. Dehydrated feed enters the ethane-recovery column (ERC) which recovers $H_2S$, ethane, and heavier components in the bottoms product. The overhead stream contains $CO_2$, methane, and any unrecovered hydrocarbons.

Propylene refrigeration at a − 10° F. level is used in the partial condenser.

Fig. 2

Seminole $CO_2$-recovery plant

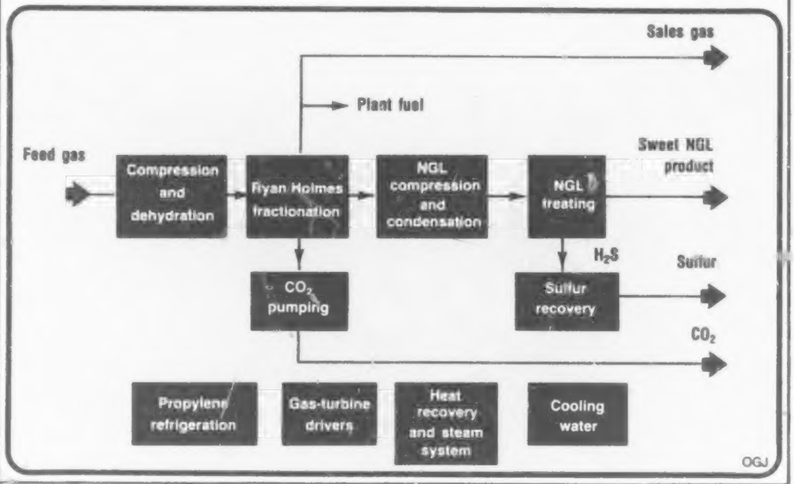
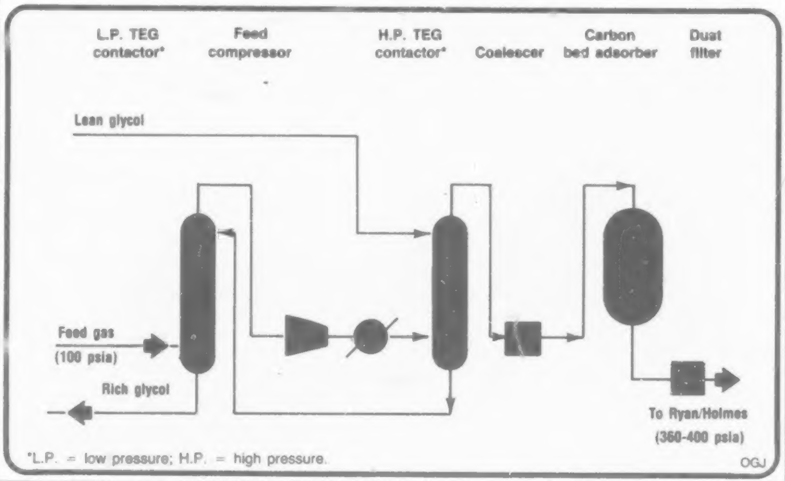

Sales gas
Plant fuel
Feed gas
Compression and dehydration
Ryan Holmes fractionation
NGL compression and condensation
NGL treating
Sweet NGL product
$H_2S$
Sulfur
$CO_2$ pumping
Sulfur recovery
$CO_2$
Propylene refrigeration
Gas-turbine drivers
Heat recovery and steam system
Cooling water
OGJ

Fig. 3

Feed-gas compression, dehydration


L.P. TEG contactor*
Feed compressor
H.P. TEG contactor*
Coalescer
Carbon bed adsorber
Dust filter
Lean glycol
Feed gas (100 psia)
Rich glycol
To Ryan/Holmes (360-400 psia)
OGJ

*L.P. = low pressure; H.P. = high pressure.

Fig. 4

Ryan/Holmes fractionation & $CO_2$ pumping

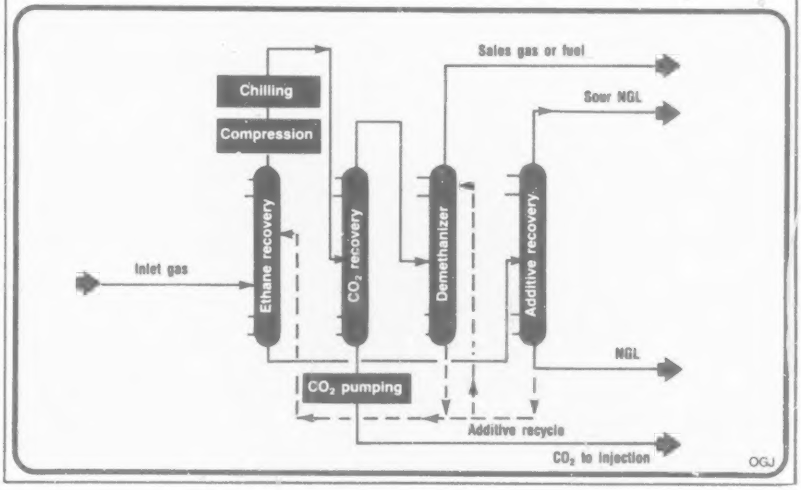

Chilling
Compression
Sales gas or fuel
Sour NGL
Inlet gas
Ethane recovery
$CO_2$ recovery
Demethanizer
Additive recovery
NGL
$CO_2$ pumping
Additive recycle
$CO_2$ to injection
OGJ

Fig. 5

ERC temp. profile

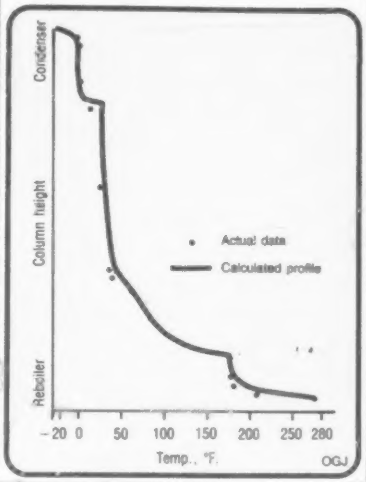


Table 4

## Actual vs. design feed conditions

| | Case A | Jan.'85 | Oct.'85 | Case B |
|---|---|---|---|---|
| Flow, MMscfd | 28.0 | 28.8 | 37.9 | 65.0 |
| Composition, mole % | | | | |
| $CO_2$ | 20.9 | 30.7 | 38.9 | 50.0 |
| $H_2S$ | 3.6 | 3.1 | 3.3 | 2.2 |
| $C_1$ | 44.2 | 42.2 | 36.5 | 27.4 |
| Balance | 31.3 | 24.0 | 21.3 | 20.4 |

Steam supplies the required reboil heat.

The ERC bottoms stream is fractionated in the additive-recovery column (ARC) to produce the circulating NGL additive stream ($C_4$+) which is used in both the ERC and demethanizer to enhance the separations there. The net ARC bottoms stream is produced as an NGL product.

The ARC overhead consists mainly of the recovered ethane and propane components together with the $H_2S$ extracted from the feed gas and some $CO_2$. This sour LPG stream can be either exported from the plant as such or sweetened to produce an LPG product and sulfur by-product.

The ERC overhead stream is compressed further in the second section of the process-gas compressor, chilled, and sent to the $CO_2$-recovery column (CRC) which produces a liquid $CO_2$ bottoms product. This liquid $CO_2$ stream is pumped to the required field-injection pressure using multistage centrifugal pumps.

The CRC reboiler exchanges against condensing propylene refrigerant. The partial condenser is refrigerated with the lowest level propylene at −45° F.

Table 5

## ERC* operation vs. design

| | Case A | Jan.'85 | Oct.'85 | Case B |
|---|---|---|---|---|
| Condenser press. | 400 psia | 380 psia | 380 psia | 400 psia |
| Overhead temp. | −5° F. | −6° F. | −13° F. | −5° F. |
| Bottoms temp. | 256° F. | 283° F. | 275° F. | 274° F. |
| $H_2S$ overhead | 50 ppm vol | 26 ppm vol | 2 ppm vol | 30 ppm vol |
| $CO_2/H_2S$ bottoms | 1.0 | 1.03 | 0.02 | 1.0 |
| $C_2$ recovery | 95% | 98% | 98% | 85% |

*Ethane recovery column

The CRC overhead stream contains about 30% $CO_2$, the remainder being methane.

The final cleanup of the CRC overhead stream is achieved in the demethanizer where NGL additive is fed to the partial condenser to obtain less than 2% $CO_2$ in the residue gas. This condenser is also operated with the coldest level of refrigeration. Demethanizer column bottoms are combined with the remainder of the NGL additive from the ARC to form the total additive stream to the ERC.

**December start-up.** Start-up operations commenced in fourth quarter 1984 following final plant mechanical construction. The process plant was thoroughly dried out with circulating nitrogen. Simultaneously, the refrigeration circuits were dried out with propylene and methanol.

Field gas was introduced to the first process train on Dec. 8, 1984. The feed gas composition at start-up is shown in Table 3. The start-up chronology was as follows:

- Dec. 8th
  - 10:00 a.m.—Feed introduced to plant
  - 1:00 p.m. —all available field gas diverted to plant
  - 5:00 p.m. —$Co_2$ to field in product line
- Dec. 9th
  - 7:00 p.m.—Residue gas on spec
  - —Light, sour NGL on spec
- Dec. 10th
  - 1:00 a.m.—ARC overhead into pipeline
  - —Residue gas into pipeline
  - 3:00 a.m.—Heavy NGL to product storage

Train 2 was started up on Feb. 12, 1985, to confirm the operability of the second train even though only one train was required to handle the feed gas volume available. The switchover was accomplished in 8 hr.

The start-up of both trains went very smoothly with less than the normal number of problems typically encountered during the start-up of such a large grassroots plant.

**High methane content.** The plant has performed well since start-up. It is interesting to compare the feed conditions experienced to date with the original design basis. Table 4 compares the January and October 1985 operations with design Cases A and B.

The $CO_2$ buildup was initially slower than expected. However, the most noticeable feature of the feed gas is the higher-than-expected methane content. This can be observed from the composition data in Table 4.

The higher methane content has a direct impact on the demethanizer operation. The demethanizer was originally sized for a residue-gas flow of 10.6 MMscfd. Any higher flows, anticipated to occur for only a short duration, were to be handled by bypassing excess column feed directly to the fuel system.

In practice, the demethanizer was found to be capable of handling the increased methane flow encountered (12.8 MMscfd in January 1985), while also maintaining residue-gas purity with respect to $CO_2$ content. The methane-$CO_2$ separation with the NGL additive was clearly demonstrated.

The ERC column has seen a wide variety of operational modes as feed conditions were changed. Table 5 shows a comparison of January and October 1985 operations with design cases A and B.

Note the high levels of ethane recovery achieved while a low level of $CO_2$ is also maintained in the bottoms. The ability of the fractionating process selectively to remove $H_2S$ from $CO_2$ is clearly evident.

The close match between measured and calculated column temperature profiles is illustrated in Fig. 3, which is based on the October 1985 observations.

Overhead product purity in actual operations (31% $CO_2$) followed closely the design VLE predictions. Column bottoms have been virtually free of methane in operations to date. The CRC column has operated in a very stable fashion.

The current mode of operation for the ARC is to maximize the net heavy NGL bottoms stream, while completely stripping out the $H_2S$. This technique produces an NGL product that passes the No. 1 copper-strip test.

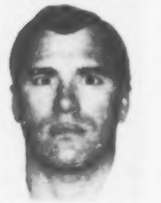
The ARC overhead stream contains 15% $H_2S$ and less than 1% $CO_2$ together with the ethane and propane components.

The Seminole plant NGL sweetening and sulfur-recovery sections were started up in August and are currently in use to treat a portion of the sour NGL product.

The balance is exported for sulfur recovery elsewhere.

The Seminole San Andres Unit $CO_2$-recovery plant, which incorporates the first commercial application of the Ryan/Holmes Technology, has been operating successfully for almost 2 years. ▪

### The authors...



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**Schaffert**

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# Integrated process offers lower gas-to-gasoline investment

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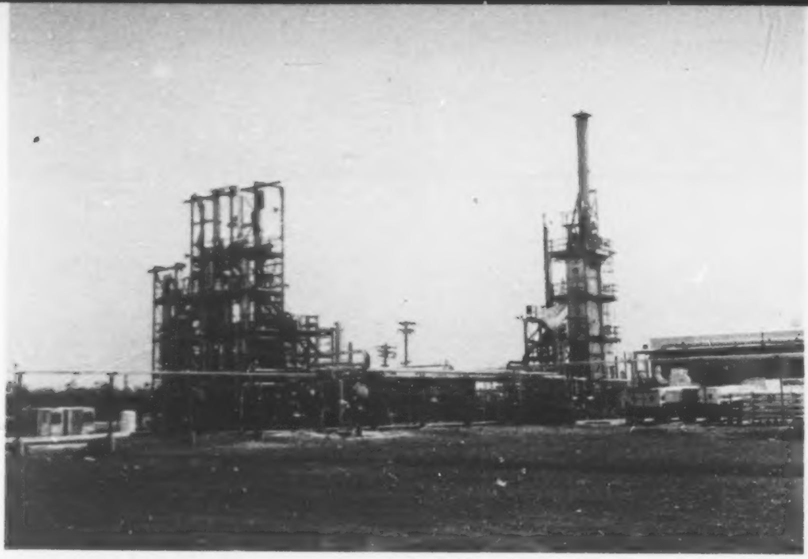


**The Houston pilot plant**, now testing the integrated syn-gas-to-gasoline process, is considered semicommercial. Scale-up to a commercial unit will be straightforward (Fig. 1).

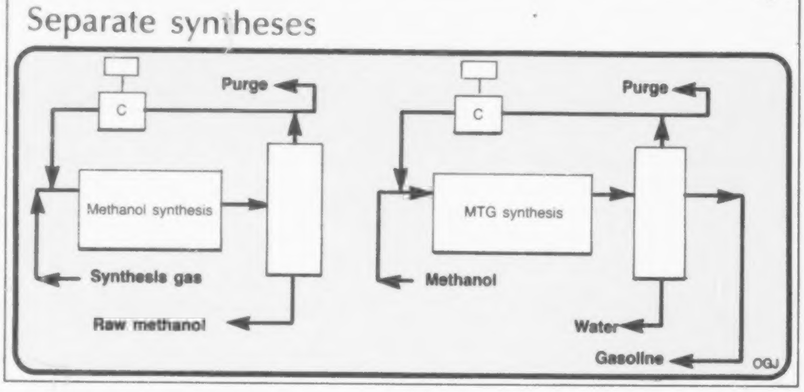


Fig. 2

Many natural gas fields are in remote locations and of a size which cannot justify construction of a pipeline or liquified natural gas (LNG) plant. In these situations, the natural gas price can be low and the manufacture of gasoline an attractive alternative to producing ammonia or other petrochemicals.

Haldor Topsøe A/S has developed an integrated process scheme to convert natural-gas-derived synthesis gas to gasoline in a single loop.

The process, Topsøe integrated gasoline synthesis (Tigas), incorporates Mobil's methanol-to-gasoline (MTG) process.

The first step is a synthesis of oxygenates. The second step is the MTG process run at conditions selected to achieve optimum operation of the integrated loop.

An industrial pilot plant has been in operation since January 1984. The plant has been running successfully, with long catalyst life, producing high-octane gasoline.

Present technology[1 2] for converting syngas into gasoline via methanol (MeOH) is carried out in two separate steps: MeOH synthesis and the gasoline synthesis (Fig. 2). MeOH is isolated as an intermediate.

Conventional methanol synthesis involves recycle of unreacted syngas at a recycle ratio of 4:1 to 5:1 because of thermodynamic limitations. Recycle is also required in the gasoline synthesis to control the temperature rise in the adiabatic gasoline reactor. These recycle operations boost energy requirements.

The MTG process is based on a shape-selective zeolite, HZSM-5, developed by Mobil.[3 4] This catalyst converts MeOH and other oxygenates to hydrocarbons in the range from $C_1$-$C_{11}$, with a high selectivity to high-octane gasoline.

During operation, the HZSM-5 is deactivated by coke formation.[5] The catalyst is regenerated by controlled burn-off of the carbon after 3-4 weeks.

In New Zealand, the first industrial plant based on the MTG process was started up successfully during October 1985.

Integration of the two syntheses into a single synthesis loop results in a simplified process scheme with lower investment and lower energy consumption.[6 7 8]

In the Tigas scheme (Fig. 4), the recycle ratio is comparable to that for conventional methanol synthesis. Additional recycle compression in the gasoline synthesis is eliminated. Furthermore, energy is saved because methanol is not condensed and reevaporated.

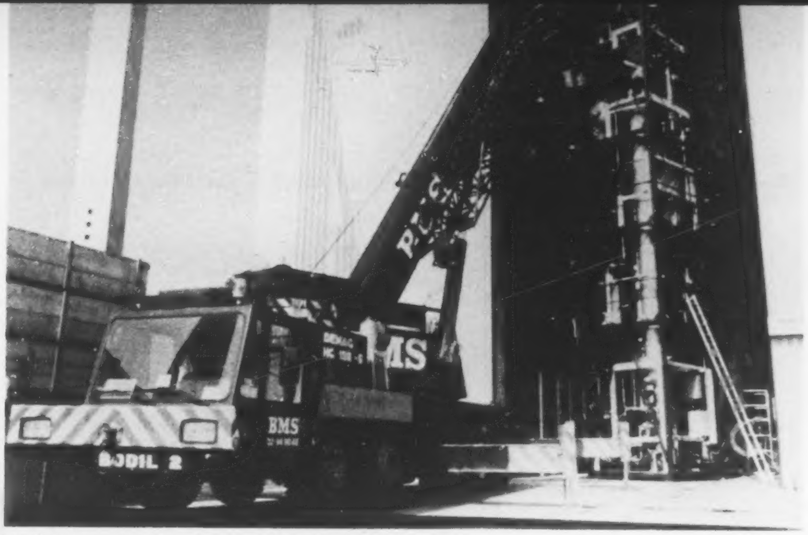
**The project.** Topsøe started development work on the integrated synthesis in the late 1970s. After successful laboratory studies, the integration was studied in a small pilot plant with a capacity of 15 kg of hydrocarbons/day. An industrial pilot plant was installed at facilities of Haldor Topsøe Inc., Houston. It started up early in 1984.

The demonstration project is sponsored by the European Economic Community. The HZSM-5 catalyst has been supplied by Mobil Research & Development Co. within an arrangement between Mobil and Topsøe. The experimental program is still under way.

Synthesis gas is provided by conventional steam reforming of natural gas and used as makeup for the gasoline synthesis loop. Natural gas containing up to 25% $CO_2$ can be used advantageously.

Coal and biomass could also be used as feedstock. Syngas from coal gasification offers the opportunity to operate the integrated syntheses at an

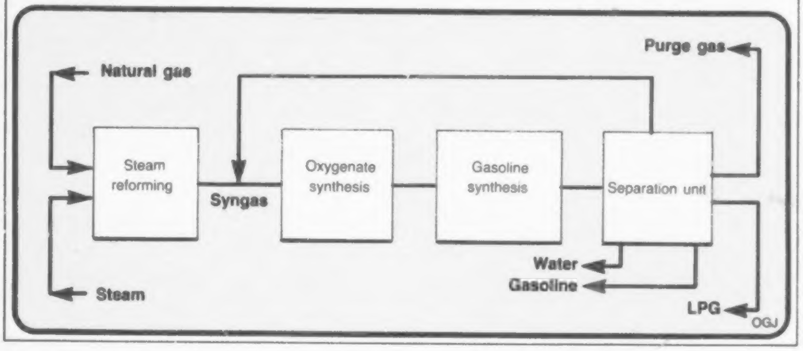
Based on a presentation made at the 6th Large Chemical Plant Conference, Oct. 9-11, 1985, Antwerp, Belgium.



**Modular construction** and a skid-mounted concept permitted the pilot plant to be shipped in standard containers. Eight containers were needed for the complete plant (Fig. 3).

Fig. 4

## Tigas process



$H_2$/CO ratio lower than for MeOH synthesis, thus saving steam.[9]

**Industrial pilot plant.** The industrial gasoline pilot plant was designed by Topsøe with a skid-mounted concept. Most of the plant was fabricated in Copenhagen and shipped to the pilot facilities site, where it was erected and connected to an existing monotube steam reformer.

The reformer had been in operation since 1980, used mainly for optimization of reformer design for operation at low steam-to-carbon ratios, and $CO_2$ reforming.[10 11]

Engineering of the gasoline unit started in the summer of 1982. The first successful test run was conducted in January 1984.

The Houston pilot plant (Fig. 1) is considered a semi-industrial unit. The flowscheme, compressors, heat exchangers, separators, piping, and instrumentation are the same as foreseen in an industrial plant. This will make the scale-up to a commercial scale plant a straightforward procedure.

In the skid-mounted concept, the steel structure was divided into several modules. Each module was the size of a standard container, convenient for land and sea transportation (Fig. 3). Eight containers were needed to transport the complete plant.

**Program and results.** The experimental program is scheduled to last for 3 years. The test program has been planned for: verification of plant performance (test run), determination of cycle length, verification of regeneration procedure, optimization of gasoline yield and quality, and final demonstration of the process scheme.

Except for some minor operational problems during the test run, the plant has been operating very satisfactorily. Several runs have been completed, with a total duration of 6,400 hr. The remaining program, to be completed early in 1987, aims at final optimization of yields and catalyst life.

**Industrial aspects.** Although the market prospects for synfuels are not attractive at present oil prices, this integrated process scheme will offer a solution to the problem of using remote and/or limited natural gas supplies, at minimum investment.

An engineering study has demonstrated that an industrial plant based on the integrated process will not involve any sophisticated equipment, nor give rise to mechanical problems. Therefore, the process will be ready for introduction to industry when final optimization of process conditions has taken place.

Because the integrated process is, in principle, an extended methanol synthesis loop, it offers the possibility of easy retrofitting of existing methanol plants to produce either gasoline or methanol.

With this concept, it is possible to switch from production of MeOH to gasoline and back. A retrofitted plant may therefore be flexible to changes in the market situation.

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*Refining Technology*

# $H_2$/thermal conversion combined for resid upgrade

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**A**s an alternative to the high investment option of reduced crude desulfurization followed by direct residual catalytic cracking, a reduced investment option combines lower severity resid desulfurization, thermal conversion, and conventional fluid catalytic cracking (FCC).

The scheme offers moderate fuel oil reduction by achieving up to 65% nondistillable conversion, a contaminant-free FCC feed (allowing the use of existing FCC facilities), and a low-sulfur fuel oil blending component.

This arrangement can be an economical first step in a staged investment strategy for bottoms upgrading, maximizing the use of existing equipment, and minimizing capital expenditures.

In the near term, price differentials between residual fuel oil and transportation fuels are expected to decline together with the price differential between light and heavy crudes. The economic justification for the investment in fuel oil upgrading facilities is thus very difficult in today's economic climate.

Table 1

## Comparison of hydrotreating operations

| | Case A RCD | Case B RCD/thermal |
|---|---|---|
| Desulfurization, wt % | 90 | 80 |
| Conradson carbon conversion, % | 60 | 48 |
| Demetallization, % | 79 | 75 |
| $H_2$ consumption, scf/bbl | Base | Base – 350 |

On the other hand, the refiner must heed the forecasts of declining residual fuel oil demand and the slowly increasing demand for middle distillates. The refiner must also accept that, looking at the longer term, the current oversupply of good quality crude is a temporary situation. In the not too distant future, refiners will be forced to process heavier crudes and implement a fuel-oil conversion strategy.

**Hydrogen addition.** Two fundamental alternatives exist for the upgrading of residual oil fractions: carbon rejection and hydrogen addition.

Carbon rejection schemes reject asphaltenes and associated contaminants such as metals, sulfur, and nitrogen, into a by-product stream with a significantly higher carbon/hydrogen weight ratio than the original feed. The resulting product stream has a lower carbon/hydrogen ratio compared to the original feed and is significantly reduced in contamination.

Alternatively, hydrogen addition schemes catalytically convert or remove contaminants by the addition of hydrogen, yielding a product stream with a lower carbon/hydrogen ratio compared to the feed without the creation of a low value by-product stream.

Historically, refiners have chosen carbon rejection schemes such as delayed coking, solvent extraction, and fluid catalytic cracking for residuum upgrading because of the relatively low operating cost of these processing alternatives. As crudes get heavier, and markets for low-hydrogen-content products (coke, asphalt, and residual fuel oil) decline, these processes become less attractive.

When a refiner wants to convert fuel oil to make only liquid products, and also to maintain or improve the quality of the remaining residual product, there is no other option. The refiner must look to hydroprocessing of the vacuum residue. The resid may be processed either by itself or as part of the atmospheric reduced crude.

Since vacuum gas oil (VGO) hydrotreating often is attractive when fluid catalytic cracking is used for conversion, hydrotreating of the atmospheric reduced crude is usually the choice.

Fig. 1

Existing refinery flow (base case)

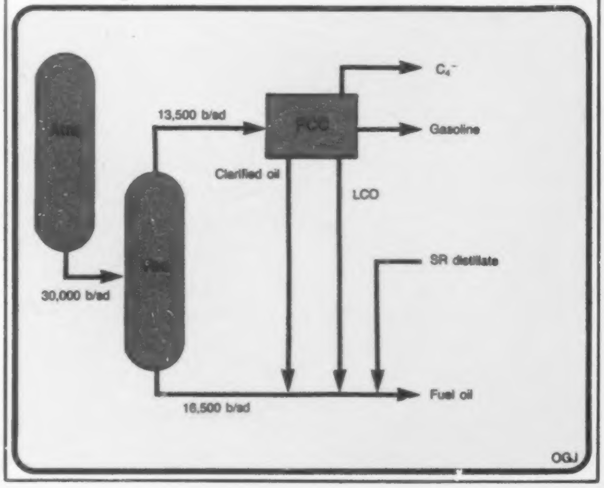
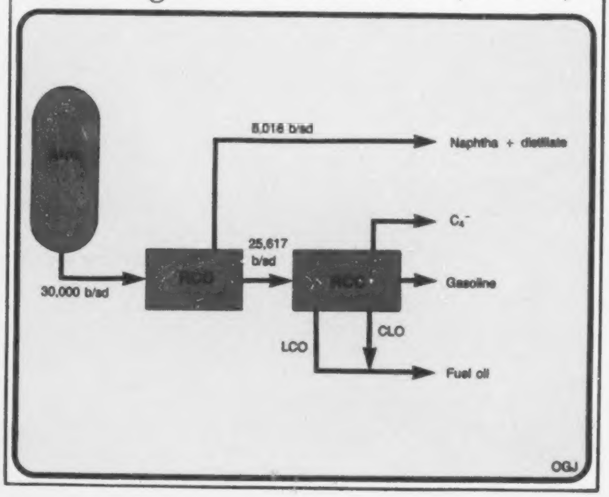


Fig. 2

Flow diagram for RCD/RCC (case A)



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Based on a Paper presented at the American Petroleum Institute 51st Midyear Refining Meeting, San Diego, Calif., May 12-15.

Table 2

## Less severe hydrotreating reduces costs

| | Case A RCD | Case B RCD/thermal |
|---|---|---|
| RCD reactor volume | Base | 0.5 Base |
| RCD reactor pressure, psig | Base | Base – 150 |
| RCD capital cost | Base | 0.75 base |
| Hydrogen plant cost | Base | 0.69 base |
| Operating cost (RCD + hydrogen plant) | Base | 0.67 base |

Table 3

## FCC feed properties

| Case: | Base | A | B |
|---|---|---|---|
| Feed data: | SR VGO | Hydrotreated reduced crude | RCD/thermal VGO |
| Charge, b/sd | 13,500 | 25,617 | 17,330 |
| Gravity, °API | 19.5 | 23.2 | 21.7 |
| Sulfur, wt % | 1.3 | 0.3 | 0.3 |
| Conradson carbon, wt % | 0.1 | 5.4 | 0.1 |
| Ni + V, ppm | nil | 7 | nil |

Because bottom-of-the-barrel hydrotreating is costly, considering the severe processing conditions and the high catalyst costs to convert the asphaltenes and organometallic compounds in the feed, the choice of processing objectives and plant design parameters can affect refining profitability significantly.

**Thermal cracking.** While thermal cracking has been used in the refining industry for more than 70 years, many refiners around the world still find thermal conversion technology an efficient and economical way to reduce fuel-oil yield or to convert heavy oils to diesel and naphtha products.

Fuel-oil reduction via thermal processing alone is limited by the stability of the cracked fuel oil. This limit can be extended by hydroprocessing of the residuum prior to thermal processing.

The combination of hydrogen addition and thermal conversion as a cost effective route to fuel oil upgrading, specifically, the thermal conversion of hydrotreated atmospheric residuum followed by vacuum fractionation for VGO recovery, is investigated.

**Processing objectives.** New, bottom-of-the-barrel upgrading facilities generally accomplish a variety of processing objectives. Many refiners are seeing an erosion of high-sulfur fuel oil markets. In addition to the overall objective of fuel-oil reduction, refiners must upgrade the quality of the unconverted fuel-oil products to meet the specifications of more stringent fuel-oil markets.

For many refiners, this translates into the production of 1.0 wt % (or lower) sulfur content fuel oil.

Facilities using fluid catalytic cracking for the primary conversion of fuel-oil blending components into gasoline and middle distillates must comply with existing and future legislation regulating regenerator flue gas $SO_x$ emissions. Of the various alternatives for flue gas $SO_x$ control, feed hydrotreating is generally considered the most viable. Current legislation relates flue gas $SO_x$ limitations to a feed sulfur level of about 0.3 wt %.

The following case studies investigate the addition of new fuel-oil upgrading facilities to an existing refinery that desires to process a heavy, medium-sulfur-content crude oil.

The following points summarize the processing objectives for this study:

- Maximum fuel oil reduction
- Maximize production of liquid products
- Decrease the refinery's gasoline/middle distillate ratio
- Unconverted fuel oil at 1.0 wt % sulfur maximum
- Feedstock to FCCUs at 0.3 wt % sulfur maximum
- Easy integration of new facilities into the existing refinery.

**Case studies.** Atmospheric reduced crude properties for the studies are summarized below:

| | |
|---|---|
| Gravity, °API | 13.4 |
| Sulfur, wt % | 2.4 |
| Conradson carbon, wt % | 11.0 |
| Asphaltenes ($C_7$ insolubles) | 3.9 |
| Ni + V, wt ppm | 27 |
| Non-distillable content (1,000° F.+) | 55 |

Two processing alternatives for fuel-oil conversion are discussed and then compared with a base case, existing refinery.

*Base case.* The existing refinery, represented in Fig. 1, is able to process 45,000 b/sd of heavy crude, which yields 30,000 b/sd of atmospheric reduced crude. The long resid is vacuum fractionated to produce

Fig. 3

Case B combination

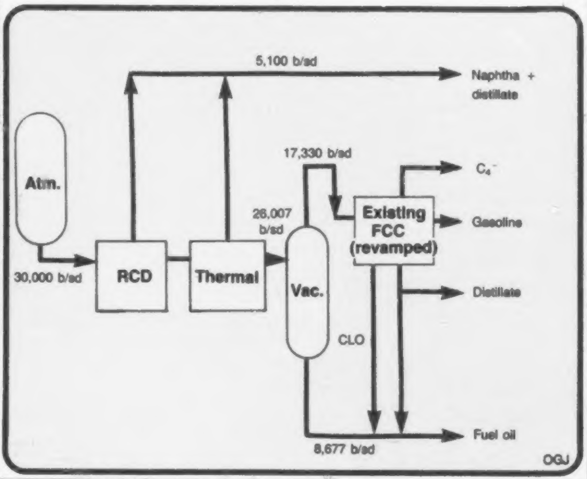
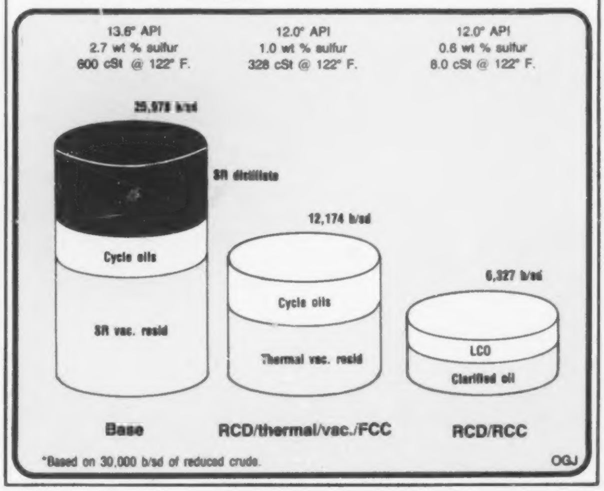


Fig. 4

Fuel oil blends*



*Based on 30,000 b/sd of reduced crude.

Table 4

## Investment cost comparison

| Case | Investment costs, $million<br>A | <br>B |
|---|---|---|
| RCD Unibon | 49.6 | 37.0 |
| Hydrogen plant | 23.5 | 16.1 |
| Thermal plant | — | 11.7 |
| Vacuum column revamp | — | 4.0 |
| FCC revamp | — | 2.0 |
| RCC | 57.3 | — |
| **Total** | **130.4** | **70.8** |

Table 5

## Process selectivities related to fuel oil

| Case | A | B |
|---|---|---|
| Flow | RCD/RCC | RCD/thermal |
| Delta fuel oil, b/sd* | −19,651 | −13,804 |
| Delta distillate, b/sd* | +10,046 | +10,178 |
| Delta gasoline, b/sd* | +11,008 | + 5,007 |
| Distillate selectivity | | |
| Delta distillate/delta fuel oil | 0.51 | 0.74 |
| Gasoline selectivity | | |
| Delta gasoline/delta fuel oil | 0.56 | 0.36 |

*Quantities related to base case.

13,500 b/sd of VGO charge to an existing FCC unit.

The 16,500 b/sd of vacuum residue are blended with light cycle oil and clarified oil from the FCCU as well as straight-run distillates to meet fuel oil viscosity specifications.

*Case A.* Case A consists of reduced crude desulfurization (RCD) followed by reduced crude catalytic cracking (RCC). The flow diagram is shown in Fig. 2. The vacuum column is eliminated and the reduced crude is routed to a new RCD Unibon unit. Naphtha and distillate products are recovered by fractionation, and the 650° F.$^{+}$ product is routed to the RCC unit for upgrading to gasoline and distillates. Clarified oil and light cycle oil are blended to produce specification fuel oil.

*Case B.* Case B combines RCD, thermal conversion, vacuum fractionation, and conventional catalytic cracking (Fig. 3). The atmospheric reduced crude is again hydrotreated in a new RCD Unibon unit. The RCD effluent is routed to a thermal conversion heater, flash vessels for naphtha and middle distillate recovery, and vacuum fractionation to recover VGO for feed to a gas-oil FCCU. Vacuum bottoms are combined with clarified oil and light cycle oil to produce specification fuel oil.

The tandem RCD/thermal conversion units perform hydrotreating and molecular weight reduction in separate sections. In so doing, high levels of nondistillable and 650° F.$^{+}$ conversion can be obtained without raising the severity of the RCD unit beyond that required for product sulfur requirements.

**Severity.** The hydrotreating severity for case A is set by the 0.3 wt % sulfur limitation on the RCC feed because the entire 650° F.$^{+}$ RCD effluent is charged to the cracking unit. A moderate level of 650° F.$^{+}$ conversion is desired to produce quality middle distillates and reduce the size of the new residual catalytic cracking unit.

This relatively stringent sulfur limitation together with the desired conversion level requires deep hydrogenation and asphaltene conversion. These are difficult reactions that require a high pressure and low liquid hourly space velocity (LHSV) operation for acceptable catalyst life.

Hydrotreating severity for Case B is set by the sulfur content of the vacuum bottoms following the thermal conversion step. Because unconverted asphaltenes and Conradson carbon bypass the FCC, hydrotreating severity is significantly reduced. Nondistillable (1,000° F.$^{+}$) and 650° F.$^{+}$ conversion is accomplished in the thermal conversion step, thus the RCD severity can be reduced even further. A high performance comparison of the two hydrotreating operations is shown in Table 1. The implications of the above severity differences on unit capital cost and operating cost requirements are shown in Table 2.

**FCC/RCC upgrading.** Table 3 shows the properties of FCC feedstocks for the three study cases.

The amount of catalytic cracking feedstock in Case A is increased by 90% relative to the base case, while the 5.4 wt % Conradson carbon content results in a 320% increase in coke burning requirement. Clearly, the existing FCCU must be replaced by a substantially larger reduced-crude conversion unit.

The VGO catalytic cracking capacity in Case B is increased by 28% relative to the base case operation. While the capacity has increased, the feed quality has improved with a reduction in sulfur content and an increase in API gravity.

An existing FCC can usually be revamped to accommodate this modest increase in hydraulic and coke burning capacity as long as the regenerator superficial velocity limits are not exceeded. In this case study, a revamp expense of $2.0 million is assumed for the addition of air blower capacity and modification to the product recovery section of the plant. Obviously, if the existing FCCU had been operating below design capacity in the base case, it may be possible to accommodate the capacity increase without any capital expenditure.

**Refinery balances.** Refinery balances were completed for the three study cases to determine the changes in yields of finished products after the implementation of the Case A or Case B upgrading equipment.

Fuel-oil blends were generated to conform to the following specifications:

| | |
|---|---|
| Gravity, °API minimum | 12.0 |
| Viscosity, cSt @ 122° F. maximum | 600 |
| Sulfur, wt % maximum, | |
| Current | 3.0 |
| Future | 1.0 |

The fuel oil in the base case meets the current sulfur specification of 3.0 wt %; the fuel oil in Cases A and B meets the future sulfur specification of 1.0 wt %. Fuel-oil blends for the three study cases are represented in Fig. 4.

The base case produces 25,978 b/sd of high sulfur fuel oil after blending vacuum residue with FCC cycle oils and straight-run distillate. This material meets the current sulfur specification of 3.0 wt %.

Case A represents maximum fuel oil reduction, reducing the fuel oil yield by 75% to 6,327 b/sd. Case B represents an intermediate degree of fuel oil upgrading, reducing the fuel oil yield by 53% to 12,174 b/sd. Both Cases A and B produce fuel oil that meet viscosity and future sulfur specifications without the use of straight-run distillate for cutter stock.

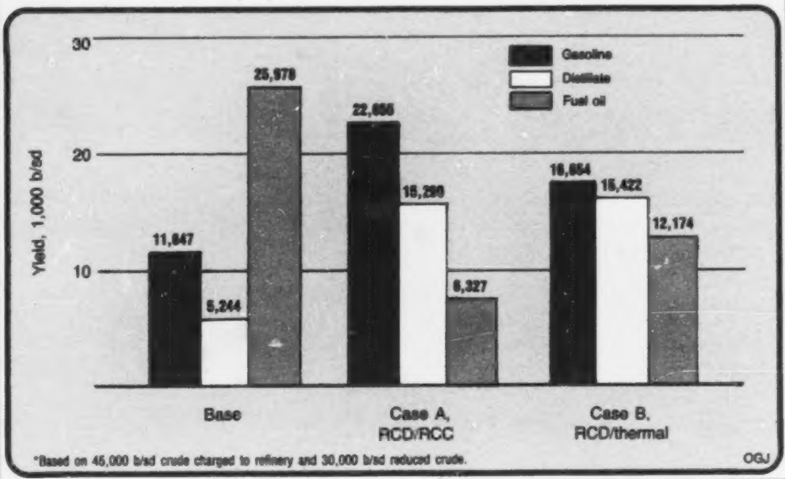
Overall refinery yields are shown in Fig. 5. The refinery's crude run is set at 45,000 b/sd to allow the production of 30,000 b/sd of atmospheric reduced crude. Straight-run distillates, catalytically reformed naphtha, and light straight-run naphtha are blended with the net products from the bottom half of the refinery.

Case A produces almost twice the gasoline yield of the base case with the aforementioned 75% reduction in fuel oil production. Gasoline plus distillate production increases by 224% relative to the base case. The gasoline-to-distillate ratio decreases from 2.2 to 1.5.

Case B shows a 90% increase in

Fig. 5

## Overall refinery yields*



*Based on 45,000 b/sd crude charged to refinery and 30,000 b/sd reduced crude.

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gasoline plus distillate production relative to the base case with a further decrease in gasoline-to-distillate ratio to 1.08.

**Capital cost.** The investment costs required to implement the Case A and Case B upgrading strategies are summarized in Table 4.

The charges for Case A include the cost of three new units: RCD Unibon, hydrogen plant, and RCC unit. The charges for Case B also include the cost of three new units: RCD Unibon, hydrogen plant, and the thermal conversion unit as well as the revamp costs of the FCC and vacuum unit.

The FCC revamp has been previously discussed. While the vacuum column feed has been reduced from 30,000 to 26,007 b/sd the VGO lift has been significantly increased from 13,500 to 17,330 b/sd. The revamp of the existing vacuum unit is assumed to cost $4 million.

**Process evaluation.** Case A, utilizing RCD and RCC technology, provides a potential ultimate in fuel oil conversion, combining hydrogen addition for contaminant removal/feedstock hydrogenation and residual catalytic cracking for effective conversion to transportation fuels.

The two processes remove sulfur, Conradson carbon, and organometallics from the reduced crude, and provide over 75% fuel oil reduction relative to the base case. This level of performance is obtained at a relatively high price, requiring the construction of two major process units and requiring an investment approaching $150 million.

Case B, combining RCD Unibon with thermal conversion technology presents a lower cost alternative, achieving a moderate degree of fuel oil upgrading at about half the capital cost of Case A.

Existing vacuum fractionation and fluid catalytic cracking facilities are utilized.

While the extent of fuel oil reduction is less than realized in Case A, the other process objectives, low-sulfur fuel oil production and low-sulfur FCC feed, are easily met. In summary, the RCD/thermal route provides:

- High levels of nondistillable and 650° F.$^+$ conversion
- Contaminant-free FCC feed after vacuum distillation
- Low-sulfur vacuum resid fuel oil blending component

The achievable nondistillable conversion from the RCD/thermal conversion combination is very much feedstock dependent. The feedstock used as the basis in this article was evaluated in UOP's pilot plants and produced approximately 65% nondistillable conversion.

Maximum conversion is related to the fuel-oil stability of the unconverted vacuum residue and thus varies with the nature of the feed.

Case B, while achieving less fuel-oil reduction relative to Case A, is more selective to middle distillate products. The two schemes achieve approximately the same increase in distillate yield. The selectivities related to fuel-oil conversion are summarized in Table 5.

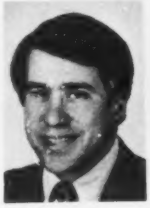
The full-range diesel product from this RCD/thermal conversion units in Case B has an acceptable cetane index of 45.

The RCD/thermal conversion strategy can be viewed as part of a staged investment strategy. The RCD unit could be designed for a future high severity mode of operation by anticipating the slightly higher pressure requirement.

At a later time, the additional catalyst volume and hydrogen plant capacity required for high severity operation could be added in conjunction with new catalytic conversion facilities to achieve maximum fuel oil conversion.

In today's economic climate, where the risk associated with fuel-oil upgrading investments and the absolute level of captial expenditure must be minimized, the RCD/thermal conversion strategy can be an attractive solution. ■

### The authors...



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# Process, hydrotreating options give olefins

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Atmospheric gas oil (AGO) has not become as important an olefins feedstock as expected. It does not appear that this will change markedly.

However, in central Europe, mildly hydrocracked vacuum gas oil (VGO) has rapidly become important. One of its advantages is that no major revamp of the AGO steam crackers is necessary. In China, sweet, straight-run paraffinic VGO is also used as an olefins feedstock (Table 1).

Now, two-stage heavy oil cracking processes have emerged, which will permit use of even heavier oils. With these processes, the first stage is low conversion precracking and product separation into a cracked oil and highly aromatic pitch. The cracked oil can be subjected to conventional tubular steam cracking.

Liquid feed steam crackers designed since the mid-1970s have almost all been capable of butane/naphtha AGO feed flexibility. Many of the older European crackers have been revamped to incorporate AGO feed processing capability. By having feed flexibility, operators have been able to benefit from seasonal and cyclical feedstock price variations. In spite of the major AGO cracking capability, AGO has not become a common feed.

In the U.S., the availability and price of gaseous feedstocks (ethane /propane) and the availability of low cost, low octane naphtha more recently have caused AGO to be used mainly only to ensure sufficient flush oil for proper primary fractionator operation by virtue of its high fuel oil yield.

In Europe, the price of AGO has not favored the widespread proliferation of AGO cracking. Some operators that initially revamped for naphtha/AGO flexibility later revamped for more propane/butane cracking capability.

Table 1

## Olefins plants in China

| Location | Capacity, thousand tons/year | Feed | Licensor/ contractor | Start-up |
|---|---|---|---|---|
| Lanzhou | 40 | Heavy oil | Kellogg revamp/ Lurgi | Initial 1969 |
| Beijing Yanshan | 300 | Gas oil | Lummus/Toyo | 1976 |
| Shanghai | 115 | Kerosine/ gas oil | Mitsubishi | 1977 |
| Liaoyang | 73 | Naphtha | IFP/TP | 1978 |
| Daqing | 300 | Gas/gas oil | S&W/JGC | Soon |
| Nanjing Yangzi | 300 | Mixed | Lummus/Toyo | Soon |
| Nanjing Jinling | 300 | Mixed | Lummus/Toyo | Soon |
| Shengli | 300 | Gas oil | Lummus/Toyo | Soon |

In Europe and in the Far East, there is relatively less demand for motor gasoline than in the U.S. Refiners have less conversion capacity.

Unlike in the U.S., VGO, also called waxy distillate, is not converted extensively and could be an attractive steam cracker feed.

**Flexibility pitfalls.** When incorporating AGO feed flexibility into a naphtha cracker, possible pitfalls can occur in the heater convection section, the indirect and direct quenching systems, the hot fractionation section, and possibly the acid gas removal system. When considering the addition of VGO cracking capability to a naphtha/AGO cracker, other problems have to be considered.

The heater convection section may run into problems of fouling due to improper vaporization as well as coking by premature cracking. There are various ways to decoke the convection section. However, it is better to prevent fouling. Coking in the cracking coil is generally faster for heavier feeds. However, since the cracking coil is designed for periodic decoking, it is already flexible with respect to feed.

With heavier feeds, the indirect quench system will foul more rapidly because of the higher fuel oil yield and lower hydrogen content of the $C_5+$ fraction. The fouling rate depends on the feed quality, cracking severity, hydrocarbon partial pressure, and high pressure (HP) steam pressure level.

Table 2 shows that certain paraffinic VGOs, e.g., Daquing, Shengli, and Libyan, have a lower density than certain naphthenic/aromatic AGOs, e.g., those of Maya and Venezuelean origin. These paraffinic VGO's do not require hydrotreating prior to tubular steam cracking in order to have an acceptable run length.

**Gas oil characterization.** Proper gas oil characterization is mandatory for development of a reliable simulation program for yield predictions. In the early days of gas oil cracking, feed characterization was basically limited to specific gravity, distillation range, and sulfur content.

In the mid-1970s Zdonik, et al., showed the usefulness of the Bureau of Mines correlation index (BMCI). In 1979, Wernicke and Kreuter outlined a rigorous analysis scheme for gas oil feed using elaborate conventional physical properties (density, TBP-curve, refractive index, etc., elemental analysis (C,H,S,N), and state-of-the-art analytical tools, e.g., nuclear magnetic resonance, structural group analysis, and mass spectrography.

Advanced laboratory tools are useful for research and development. However, for routine operations the minimum number of properties readily available from crude assays is preferable. For AGO, the common crude assays provide a distillation curve, density, sulfur content, pour point, aniline point, viscosity, refractive index, cetane, and diesel index. For heavy gas oil (Table 5), Conradson carbon and nitrogen content are also available.

Cetane index (ignition quality) is not usually used for chemical feed characterization. Pour point and aniline point are not as frequently used for gas oil characterization as for

# plants more heavy-oil-cracking flexibility

Table 2

## Gas oil characteristics*

| | Arabian Light | Zueitina (Libya) | Daqing (China) | Shengli (China) | Brent (No.Sea) | Maya (Mexico) |
|---|---|---|---|---|---|---|
| Range, °C. | 235-343 | 232-343 | 260-335 | 260-349 | 235-350 | 260-343 |
| Sp gr 15/15° C. | 0.838 | 0.833 | 0.829 | 0.851 | 0.846 | 0.873 |
| Sulfur, wt % | 0.72 | 0.24 | 0.039 | 0.53 | 0.1 | 2.17 |
| Pour point, °C. | −12 | −4 | 4 | 4 | −12 | −1 |
| Aniline Point, °C. | 70 | 77 | 82 | - | 71 | 67 |
| Heavy | | | | | | |
| Range, °C. | 343-565 | 343-538 | 412-500 | 415-565 | 350-550 | 343-593 |
| Sp gr 15/15° C. | 0.903 | 0.881 | 0.868 | 0.905 | 0.898 | 0.944 |
| Sulfur, wt % | 1.83 | 0.36 | 0.11 | 0.79 | 0.57 | 3.14 |
| Pour point, °C. | 35 | 38 | - | 43 | 39 | 41 |
| Aniline point, °C. | 88 | - | 47 | 94 | - | 75 |
| Con carbon, wt % | - | 0.18 | 0.03 | 0.28 | 0.29 | 0.69 |

*Gas oils from Shengli and Daqing (Taching) have a relatively low density.

Table 3

## Associated hydrocracker/steam crackers

| Operator/site | Process licensors | | Ordered |
|---|---|---|---|
| | Hydrocracker | Steam cracker | |
| URBK, West Germany | Union Oil | Lummus | Started with old unit |
| Neste Oy, Finland | Union Oil | Lummus/staff | |
| VEBA, West Germany | BASF/IFP | Linde | 1982 |
| Shell/ROW, West Germany | Shell | Linde/Shell | 1982 |
| Idemitsu, Japan | BASF/IFP | MW Kellogg | 1982 |
| Total/Dow, France | Union Oil | — | 1984 |
| Leuna, East Germany | Union Oil | Lummus | 1984 |
| Most, Czechoslovakia | Union Oil | Lummus | 1984 |
| Slovnaft, Czeckoslovakia | Union Oil | Lummus | 1984 |
| Dr. Grotewohl, East Germany | — | Linde | 1985 |

chemical feed evaluation.

The more common methods of gas oil feed characterization are based on the use of density, distillation curve, sulfur and nitrogen content, and frequently refractive index, viscosity, and aniline point.

**VGO as olefins feed.** With the demand for middle distillates high, the transfer price for VGO is usually considerably lower than for AGO. However, VGO usually has a considerably lower hydrogen content than AGO from the same crude. Therefore, VGO has lower olefins and higher pyrolysis fuel oil (PFO) yield.

The main problem with steam cracking nonhydrotreated VGO is that for practical cracking severity the fouling rate of the indirect quench system is so high that the operation is impractical.

This does not apply to paraffinic VGOs, e.g., those of Daqing, Shengli, and Libyan origin. These paraffinic VGOs have high olefins yield, and the fouling rate of the indirect quench system is comparable to Middle East AGO. For this reason, the Nanjing Yangzi steam cracker will be operating on straight run, low sulfur, paraffinic Shengli VGO although there is a hydrocracker within the complex.

Tubular steam cracking of VGO without indirect quenching is possible. Esso (Port Jerome, France) was cracking nondesulfurized Middle East VGO in a facility without an indirect quench system in the early 1970s. However, a steam cracker without an indirect quench system has fairly high energy consumption. This operation is certainly not economical for naphtha feed.

Since the mid-1970s, various process licensors of hydrocracking proceses (Linde, Union Oil/Lummus, IFP, Shell) have promoted mild hydrocracking of the VGO prior to steam cracking. In the late 1970s, this approach was applied for the first time on a commercial scale.

Some German companies used old equipment for hydrocracking reactors. A dedicated hydroconverter was only used to prepare steam cracker feeds.

Now that the technology has matured, operators of integrated refineries and steam crackers have installed conventional single or two-stage hydrocrackers which can be used for steam cracker feed preparation as well as hydrocracking for middle distillates.

Shell built a single-stage, mild hydrocracker mainly for the production

Table 4

## Heavy oil processes for olefins

| Process (Licensor) | Cracking stages | Concept | Feedstock | Status |
|---|---|---|---|---|
| BASF, fluid bed | 1 | Fluid bed | Crude | A |
| ACR* (Kureha/UCC) | 1 | Hot flame | Paraffinic naphtha to GO | Demo A |
| PCC Dow | 1 | Hot flame | Heavy oil | Demo A? |
| Japan KK | 1 | Coke heat carrier | Residue | Demo I/A |
| TRC (S&W/Gulf) | 1 | Hot diluent/ fluid bed | Heavy oil | |
| Cosmos Mitsui | 1 | Molten salt | Heavy oil | Pilot A? |
| Various tubular | 2 | Hydrocracking/tubular | Vacuum gas oil | In operation |
| Eureka | 2 | Precracking/ tubular | Residue | In operation |
| Two-stage pyrolysis | 2 | Precracking/ tubular | Residue | Pilot |
| IHOP(S&W/Asahi Chemical) | 2 | Precracking | Heavy oil | Demo 1986 |

*Union Carbide Corp.

Key:

A = Abandoned

I = Interrupted

Table 6

## Chinese steam cracker characteristics and yields

| Main products* | wt % |
|---|---|
| $CH_4$ | 10.01 |
| $C_2H_4$ | 24.30 |
| $C_2H_6$ | 4.00 |
| $C_3H_6$ | 16.38 |
| $C_4H_6$ | 5.37 |
| $C_5$s | 6.58 |
| Coil design: | 4-2-1 pass split coil |
| Steam dilution, kg/kg: | 0.75 |
| Crude origin: | Renqui (North China) |
| Feed: | Kerosine/AGO mix |
| Feed specification: | |
| Sp gr 20/4° C. | 0.8144 |
| ASTM distillation, °C. | |
| IBP | 175 |
| 50 vol % | 284.5 |
| FBP | 331.5 |
| Sulfur, wt % | <0.04 |
| PONA | |
| Parafins/olefins | 71 |
| Naphthenes | 22.5 |
| Aromatics | 6.5 |
| Refractive index (20° C.): | 1.4563 |

*PHENICS process simulation

Table 5

## Vacuum residue characteristics

| | Shengli | Arabian Light | Khursaniyah | Kuwait |
|---|---|---|---|---|
| Range, °C. | 500+ | 565+ | 565+ | 538+ |
| Sp gr, 15/15° C. | 0.98 | 0.994 | 1.038 | 1.035 |
| Pour point, °C. | <50 | 27 | 46 | — |
| Sulfur, wt % | 1.4 | 2.88 | 5.35 | 5.11 |
| Conradson carbon, wt % | 13.9 | 16.2 | 23.3 | 21.9 |

of hydrogenated/cracked waxy distillate in Godorf, West Germany.

The VGO yield is some 45%. There is also a 30% yield of middle distillate, 10% naphtha, and 6% kerosine. Hydrogen consumption is about 16 kg/ton VGO. Yields from cracking mildly hydrocracked VGO can be fairly similar to naphtha cracking. A VGO hydrocracker operating at high pressure requires considerable investment. A possible lower-cost route is to replace the catalyst in a VGO hydrodesulfurization unit with a mild hydrocracking catalyst. In central Europe, quite a few companies have opted for VGO feed flexibility by building a VGO hydrocracker (Table 3).

**Single-stage cracking.** Until quite recently, the cracking of crude oil to lower olefins was not considered attractive for nonintegrated petrochemical companies. There are many technical problems. Crude oils, and particularly residues, contain asphaltenes, which are well known coke precursors. For a long time, only nontubular pyrolysis processes were considered for heavy oil feeds.

A crude oil cracking process in operation until about 1970 was the BASF fluid-bed process (Table 4). The feed was a paraffinic crude oil.

The advanced cracking reactor (ACR) developed by Union Carbide Corp., Kureha, and Chiyoda, was initially intended for crude oil feedstock. More recently, feedstocks ranging from naphtha to VGO have been suggested.

The original ACR process employed superheated steam at 2,000° C. The later version is a high temperature flame cracking process. At the higher reaction temperature, the acetylene and ethylene yields are high. The propylene yield is lower than for tubular steam cracking.

Dow's PCC process also operates at a high temperature. Therefore, yields are significantly different from steam cracking.

The Japanese Kunugi/Kunii (KK) coke fluidized-bed process has also been tested with vacuum residue feedstock on a semicommercial scale. The residence time is as high as 3 sec. Consequently, yields are not impressive. Stone & Webster and Gulf's TRC process features lower investment than tubular cracking and excellent fuel flexibility. However, the process is most economical at low propylene /ethylene (P/E) ratios. Operators currently want a high P/E ratio.

Although several of these nontubular processes have been tested on a semicommercial scale, none have been used either to revamp an existing cracker or in a new cracker.

One way to use heavy oils, i.e., vacuum residue, as an olefins feedstock is to adopt a new cracker design. Another way is to pretreat the heavy oil to suit established tubular steam crackers. This is comparable to the mild hydrocracking of VGO.

**Dual-stage cracking.** The structural analysis of vacuum residues by $C_{13}$ NMR spectroscopy has shown the presence of significant amounts of long paraffinic straight chains. Therefore, this residue has reasonable potential as an olefins feedstock. However, it also contains some weight percent of asphaltenes, concentrated by distillation. As asphaltenes are well known coke precursors, the residue is unfit for direct tubular cracking.

The Eureka process of Kureha Chemical is based on thermal cracking of vacuum residue at some 490° C. and atmospheric pressure, with continuous stripping by superheated steam. The products are 30% pitch, 65% cracked oil, and 5% gas.

Continuous steam stripping makes the process essentially different from such conventional cracking processes as visbreaking. Continuous steam stripping suppresses poly-condensation.

When the cracked oil product is pyrolyzed, reasonable olefins yields can be obtained, depending on the initial crude oil quality. For this reason, the Eureka process has also been promoted for preparing steam cracker feed from residue.

However, the cracked oil product contains minor amounts of carbon residue and asphaltenes. The asphaltenes in the cracked oil may jeopar-

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dize the furnace/transfer line exchanger run length.

In the final Nanjing Yangzi flowscheme (Fig. 1), the cracked oil from the 20,000 b/d Eureka residue conversion unit is sent to the hydrocracker and not used for steam cracking. Yields from the conventional steam cracking unit are given in Table 6. In a two-stage concept, atmospheric or vacuum residue is cracked in the first stage at low severity. The pitch and cracked oil are separated.

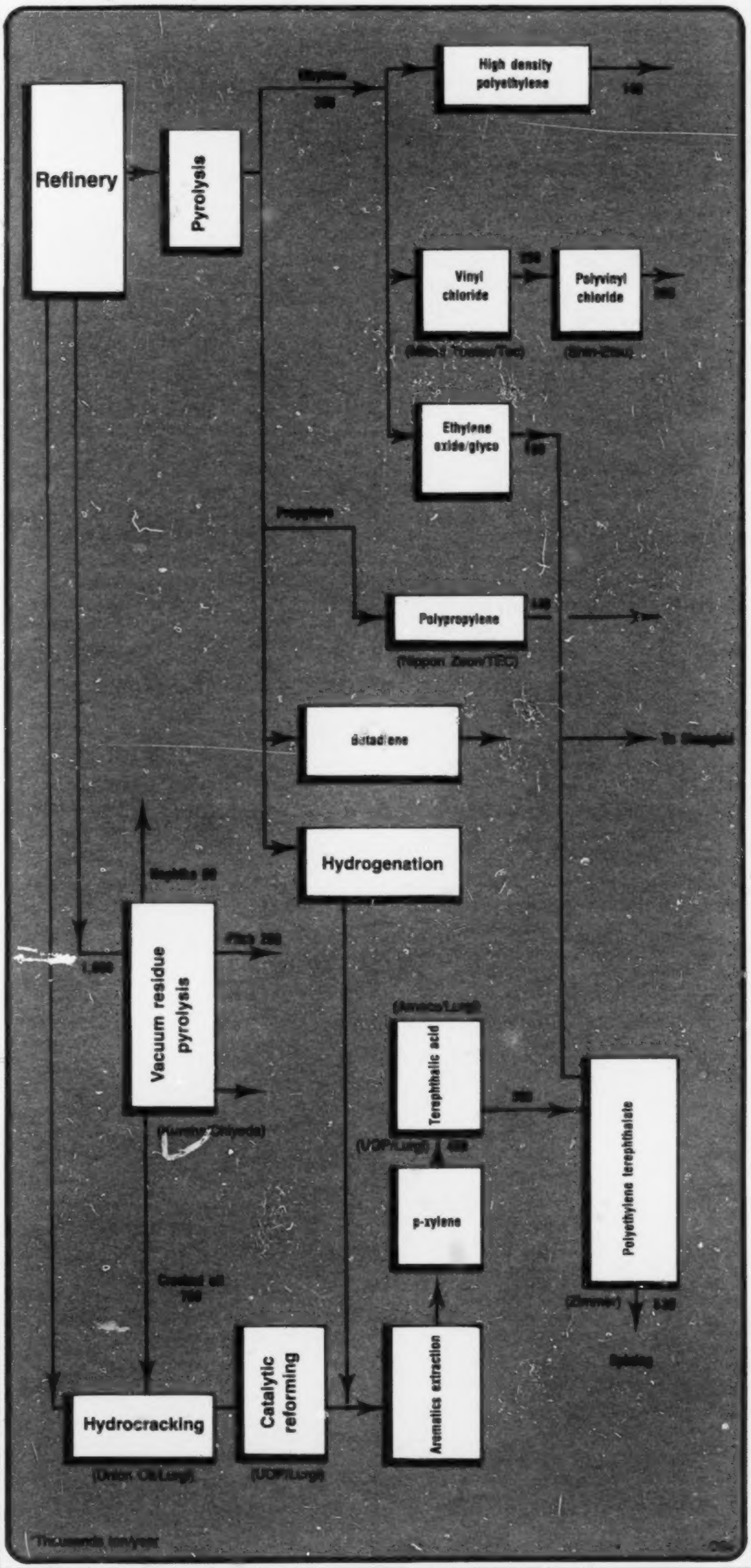
The aromaticity of the cracked oil is much lower than for the feed. Analysis has shown that the cracked oil product contains long, paraffinic straight chains similar to the original vacuum residue.

The cracked oil can be distilled easily. It is then steam cracked under more or less conventional conditions. The once-through yield is 26.5 wt % ethylene and 11.7 wt % propylene for Daqing vaccuum residue.

This clearly demonstrates that dual-

Fig. 1

Nanjing Yangzi Petrochemical Co. flow scheme *


Refinery
Pyrolysis
High density polyethylene
Vinyl chloride
Polyvinyl chloride
Ethylene oxide/glyco
Polypropylene
(Nippon Zeon/TEC)
Butadiene
Hydrogenation
Vacuum residue pyrolysis
(Amoco/Lurgi)
Terephthalic acid
(UOP/Lurgi)
p-xylene
Polyethylene terephthalate
Hydrocracking
Catalytic reforming
Aromatics extraction
(UOP/Lurgi)

*Thousands ton/year

stage cracking can be attractive for heavy oil feedstocks. However, to avoid the problems associated with tubular cracking of feedstocks containing asphaltenes, straight-run vacuum residue will probably not be used in this early stage of development. Deasphalted, preferably paraffinic, residues will be used.

The feature of this dual-stage concept is that well-established, tubular cracking technology can be used, even with deasphalted residue as feedstock. This seems preferable to using unconventional pyrolysis technology which has only been proven on a small scale, for a limited time, and frequently with a different product slate.

With the two-stage technology, it is basically possible to revamp existing naphtha/AGO crackers to accept heavy oil feedstock. Such a revamp would include adding a suitable residue precracking/oil-pitch separation process, and possibly a hydrodesulfurization unit, and revamping the cracking furnace. A suitable precracking process for the first stage would be the Eureka thermal cracking process with continuous steam stripping.

The main advantages of two-stage cracking are the feasibility of using low cost heavy oil feedstock and well-proven tubular cracking technology. There is no need for unconventional processing steps.

When dual cracking seems the best way to use residue as an olefins feed, the next step is proper integration of the cracking steps for energy conservation and savings on equipment, investment, and plot area. Recently, Stone & Webster and Asahi Chemical Co. announced a joint development to crack heavy oil by an integrated process called integrated heavy oil pyrolysis (IHOP).

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# Transfer-line design uses special procedures

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Fluid catalytic cracking (FCC) and fluid coking units utilize large-diameter, high-temperature piping systems to transfer fluidized catalyst, coke fines, and hot gases between process vessels. Because of the large diameters and high temperatures, these transfer lines require special design procedures and considerations. The designs are beyond the scope of industry piping standards.

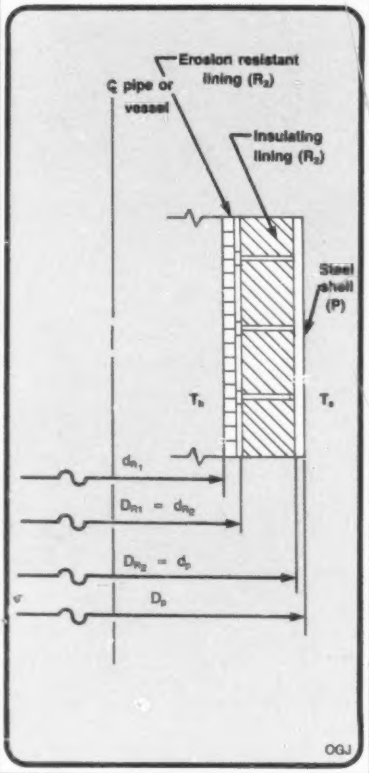
A complete stress analysis is required for each line with considerations given to thermal expansion, dead load (wind, seismic, etc.), flow-induced vibrations, allowable equipment loads, vessel nozzle connections, support and restraint devices, and special piping components such as valves, flanges, and expansion joints. Any state of-the-art computer program can be used to calculate deflection and stresses for the various conditions.

Before the analysis can begin, all the possible process conditions need to be known so that the analyst can consider the most economic combination of pipe material and refractory lining. The metal temperature of the pipe will have to be determined by calculating the heat loss through the refractory layers.

Moment of inertia, density, and pipe-wall thickness have to be modified to include the increased stiffness and weight effects of the refractory lining in the computer analysis. The input to the flexibility program is straightforward for most lines, but for transfer lines, the input is the result of careful evaluation and lengthy calculations.

Fig. 1

Refractory calculations



**Material selection.** Process temperatures in transfer lines can range from 900° F. to 1,600° F. with possible short-term upset temperatures exceeding 1,800° F. This requires the use of either high-temperature alloy material such as 321 stainless steel, or internal refractory lined carbon steel.

There are advantages and disadvantages to both types of material selection. Lines using high-temperature alloy pipe are smaller in outside diameter and do not have to be designed to carry the added weight of refractory. They can also be fully insulated for maximum heat conservation.

However, the material costs are higher than carbon steel pipe, and the allowable stress values for alloy pipe at elevated temperatures decrease significantly. Furthermore, brittle sigma phase formation, polythionic stress corrosion, chloride attack, and creep are undesirable effects which may cause problems in high-temperature alloy lines.

The high metal temperatures also cause thermal expansion problems that can create the need for highly sophisticated expansion joints. This can greatly increase the cost for these systems, and may reduce the run length of the unit.

In piping systems using internal refractory lining, the steel shell is insulated from the process fluid, permitting the use of carbon steel materials at much lower temperatures. The lower metal-skin temperatures greatly reduce the internal piping stresses, and in most cases, will eliminate the need for costly expansion joints.

However, the refractory lining must be periodically inspected. It cannot be used in lines attached to sensitive equipment, such as expander inlet lines, where substantial damage may occur should refractory pieces break loose and enter the equipment.

In lines that transfer catalyst of coke fines, erosion is a problem. A refractory with high erosion resistance must be used. This type of lining has a low insulating value and requires an increase in thickness to hold down piping skin temperatures and heat loss.

Where heat loss must be kept to a minimum, a dual layer lining can be used made up of a thinner layer of erosion-resistant lining backed by a thicker layer of insulating refractory. The type and thickness of refractory being used must be determined before the diameter of the line can be sized.

**Flexibility and support.** One of the most difficult problems in designing high-temperature transfer lines is providing adequate flexibility and proper support to minimize piping stresses and equipment connection loads. A thorough understanding of the operating conditions is required to properly determine the thermal interaction between the process vessels and the interconnecting pipe.

The shell temperatures of the vessels and pipe with refractory lining must be calculated using appropriate

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TYPE     MATERIAL      REF    T1      K1      T2      K2      T3      K3    LB/FT3     PSI
MMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMMM
  1    CARBON STEEL     1     100  358.80     500  319.20    1000  256.80   489.54    6113
  2    LOW CHROME       1     100  258.00     500  260.40    1000  229.20   489.54    6998
  3    STAIN. STEEL     1     100  104.40     600  135.60    1200  168.00   499.33    5907
  4    MINER. FIBER     0     100    0.27     400    0.50     600    0.71     8.00       0
  5    CALCIUM SIL.     0     300    0.37     500    0.51     700    0.56    12.00       0
  6    RESCO AA-22      2     500   10.20    1000   10.30    1500   10.40   170.00    1800
  7    RESCO RS-17E     2    1000    7.10    1500    7.30    2000    7.50   136.00    1550
  8    RESCO RS-3       2     500    1.85    1000    1.90    1500    2.35    85.00     400
  9    C.E. AR-400      6     500    8.60    1000    7.40    1500    5.60   170.00    1850
 10    BW K-TUF CV      4     500    6.78    1000    6.83    1500    7.02   140.00    1550
 11    GFC LC75-28G     0     500    2.50    1000    2.70    1500    2.85    96.00     400
 12    GR LO-ABRADE     0     800    4.60    1200    4.81    1600    5.03   133.00    1400
 13    GR CAST-26L      0     800    1.79    1200    1.87    1600    1.89    50.00      40
 14    HW LW-CAST22     0     500    1.44    1000    1.63    1500    1.86    56.00     140
 15    HW THERMAX       3     500    6.00    1000    6.00    1500    6.00   126.00     810
 16    BW 2500HS        0     500    2.50    1000    2.50    1500    2.50    75.00     200
 17    K = 7.00         4     500    7.00    1000    7.00    1500    7.00   150.00    1300
 18    HW LW-ES         3     500    2.40    1000    2.58    1500    2.70    80.00     400
```

**Properties** of commonly used pipe are stored in a library (Fig. 2).

heat-transfer methods. All operating, start-up, and upset conditions must be considered.

In addition to the variations in process fluid temperatures, the exterior metal shell temperature can fluctuate as much as 400° F. between extreme summer and winter ambient conditions. This causes a broad range of thermal conditions which needs to be considered in the stress analysis.

In many cases, the internal stresses will reverse between summer and winter conditions, requiring that the stresses from both conditions be added together to determine the complete stress range.

Wind velocity must also be considered in the calculation of the metal shell temperature.

In order to analyze the system thermally, the metal (surface) temperature of the pipe must be determined. The following procedure outlines a method which can be used to calculate the surface temperature (Fig. 1).[1]

1. Assume a surface temperature ($T_s$) of the pipe and calculate the heat loss ($Q_1$) using:

$$Q_1 = 0.174 \times E\left[\frac{(T_s + 460)^4}{100} - \frac{(T_a + 460)^4}{100}\right] + 0.296\,(T_s - T_a)^{1.25}\left(\frac{V + 69}{69}\right)^{0.5} \quad (1)$$

where:

$Q_1$ = Q = Heat loss, BTU/sq ft-hr

E = Surface emissivity

$T_s$ = Surface temperature, °F.

$T_a$ = Ambient temperature, °F.

V = Wind velocity, ft/min

2. Calculate the heat loss, Q, using:

$$Q = \frac{T_h - T_a}{\frac{D}{2}\left[\Sigma \frac{\log_e (d_{i+1}/d_i)}{K_i}\right] + \frac{T_s - T_a}{Q_1}} \quad (2)$$

where:

$d_i$ = Inside diameter of pipe or refractory layer, in.

D = Outside diameter of pipe, in.

$K_i$ = Conductivity of layer (i), BTU/sq ft-hr-°F./in.

$T_h$ = Fluid temperature, °F.

3. Calculate the surface temperature, ($T_s$) using:

$$T_s = T_h - \left\{\frac{QD}{2}\left[\Sigma \frac{\log_e (d_{i+1}/d_i)}{K_i}\right]\right\} \quad (3)$$

4. Repeat Steps 1 through 3 until Q = $Q_1$. Normally three or more iterations are required.

The ability of the piping system to absorb the differential expansion in lines with internal refractory is decreased due to the added stiffness of the internal lining. In order to accurately calculate the stresses and reaction loads, this stiffness should be accounted for in the flexibility analysis.

The density of the refractory must also be included in the weight analysis to properly size pipe supports. Most computer analysis programs consider only the effect of the pipe when calculating the physical properties of the system.

Therefore, the properties of the pipe must be modified before the computer analysis is made. The following procedure outlines a method which can be used to calculate the equivalent properties (Fig. 1).

1. Calculate the moments of interia, (I), of the pipe and internal refractory layers:

$$I_i = \frac{\pi}{64}(D_i^4 - d_i^4) \quad (4)$$

where:

$I_i$, $I_p$, $I_{R1}$, $I_{R2}$, ... = Pipe and refractory layers, respectively, in.[4]

$D_i$ = Outside diameter of pipe or refractory layer, in.

$d_i$ = Inside diameter of pipe or refractory layer, in.

2. Calculate the equivalent moment of inertia, ($I_e$), and the equivalent stiffness, ($E_e$), of the combined pipe and refractory:

$$I_e = \frac{E_p I_p + \Sigma E_{R_i} I_{R_i}}{E_p} \quad (5)$$

$$E_e = \frac{E_p I_p + \Sigma E_{R_i} I_{R_i}}{I_p} \quad (6)$$

where:

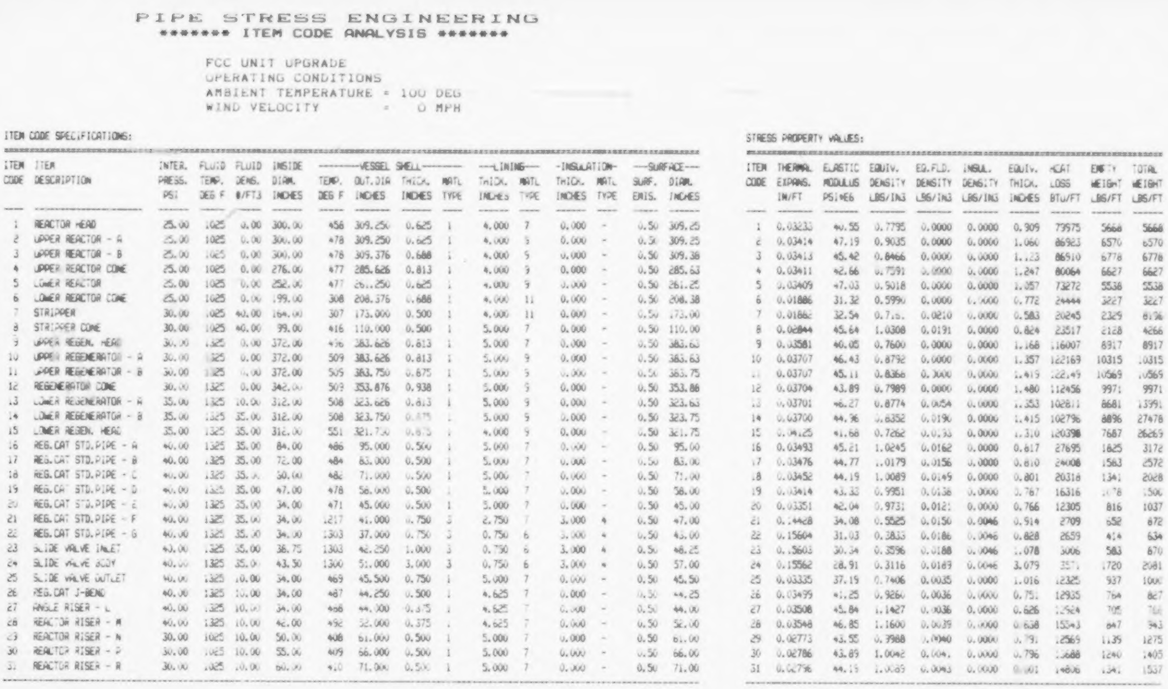
$E_p$ = Modulus of elasticity of the pipe, psi

$E_{R_i}$ = Modulus of elasticity of the refractory layer, psi

3. Using the value for $I_e$, calculate an equivalent pipe wall thickness, ($T_e$):

$$T_e = 0.5\left[D_p - \left(D_p^4 - \frac{64\, I_e}{\pi}\right)^{0.25}\right] \quad (7)$$

This value is used to determine the flexibility factor, (K), and stress intensification factors, ($i_i$, $i_o$), for miters and bends from the equations in ANSI



```
           P I P E   S T R E S S   E N G I N E E R I N G
               ******* ITEM CODE ANALYSIS *******

                   FCC UNIT UPGRADE
                   OPERATING CONDITIONS
                   AMBIENT TEMPERATURE = 100 DEG
                   WIND VELOCITY       =   0 MPH

ITEM CODE SPECIFICATIONS:
==================================================================================================================
ITEM ITEM                    INTER.  FLUID FLUID  INSIDE   ---------VESSEL SHELL---------  ---LINING---  -INSULATION-  ---SURFACE---
CODE DESCRIPTION             PRESS.  TEMP. DENS.  DIAM.    TEMP.  OUT.DIA  THICK.  MATL    THICK.  MATL  THICK.  MATL  SURF.  DIAM.
                             PSI     DEG F #/FT3  INCHES   DEG F  INCHES   INCHES  TYPE    INCHES  TYPE  INCHES  TYPE  EMIS.  INCHES
---- ---------------------   ------  ----- -----  ------   -----  -------  ------  ----    ------  ----  ------  ----  -----  ------
  1  REACTOR HEAD            25.00   1025   0.00  300.00    456   309.250  0.625    1      4.000    7    0.000    -    0.50  309.25
  2  UPPER REACTOR - A       25.00   1025   0.00  300.00    478   309.250  0.625    1      4.000    5    0.000    -    0.50  309.25
  3  UPPER REACTOR - B       25.00   1025   0.00  300.00    478   309.376  0.688    1      4.000    5    0.000    -    0.50  309.38
  4  UPPER REACTOR CONE      25.00   1025   0.00  276.00    477   285.626  0.813    1      4.000    9    0.000    -    0.50  285.63
  5  LOWER REACTOR           25.00   1025   0.00  252.00    477   261.250  0.625    1      4.000    9    0.000    -    0.50  261.25
  6  LOWER REACTOR CONE      25.00   1025   0.00  199.00    308   208.376  0.688    1      4.000   11    0.000    -    0.50  208.38
  7  STRIPPER                30.00   1025  40.00  164.00    307   173.000  0.500    1      4.000   11    0.000    -    0.50  173.00
  8  STRIPPER CONE           30.00   1025  40.00   99.00    416   110.000  0.500    1      5.000    7    0.000    -    0.50  110.00
  9  UPPER REGEN. HEAD       30.00   1325   0.00  372.00    496   383.626  0.813    1      5.000    7    0.000    -    0.50  383.63
 10  UPPER REGENERATOR - A   30.00   1325   0.00  372.00    509   383.626  0.813    1      5.000    9    0.000    -    0.50  383.63
 11  UPPER REGENERATOR - B   30.00   1325   0.00  372.00    505   383.750  0.875    1      5.000    5    0.000    -    0.50  383.75
 12  REGENERATOR CONE        30.00   1325   0.00  342.00    509   353.876  0.938    1      5.000    5    0.000    -    0.50  353.88
 13  LOWER REGENERATOR - A   35.00   1325  10.00  312.00    508   323.626  0.813    1      5.000    9    0.000    -    0.50  323.63
 14  LOWER REGENERATOR - B   35.00   1325  35.00  312.00    508   323.750  0.875    1      5.000    5    0.000    -    0.50  323.75
 15  LOWER REGEN. HEAD       35.00   1325  35.00  312.00    551   321.750  0.875    1      4.000    9    0.000    -    0.50  321.75
 16  REG.CAT STD.PIPE - A    40.00   1325  35.00   84.00    486    95.000  0.500    1      5.000    7    0.000    -    0.50   95.00
 17  REG.CAT STD.PIPE - B    40.00   1325  35.00   72.00    484    83.000  0.500    1      5.000    7    0.000    -    0.50   83.00
 18  REG.CAT STD.PIPE - C    40.00   1325  35.00   60.00    482    71.000  0.500    1      5.000    7    0.000    -    0.50   71.00
 19  REG.CAT STD.PIPE - D    40.00   1325  35.00   47.00    478    58.000  0.500    1      5.000    7    0.000    -    0.50   58.00
 20  REG.CAT STD.PIPE - E    40.00   1325  35.00   34.00    471    45.000  0.500    1      5.000    7    0.000    -    0.50   45.00
 21  REG.CAT STD.PIPE - F    40.00   1325  35.00   34.00   1217    41.000  0.750    3      2.750    7    3.000    4    0.50   47.00
 22  REG.CAT STD.PIPE - G    40.00   1325  35.00   34.00   1303    37.000  0.750    3      0.750    6    3.000    4    0.50   43.00
 23  SLIDE VALVE INLET       40.00   1325  35.00   36.75   1303    42.250  1.000    3      0.750    6    3.000    4    0.50   48.25
 24  SLIDE VALVE BODY        40.00   1325  35.00   43.50   1300    51.000  3.000    3      0.750    6    3.000    4    0.50   57.00
 25  SLIDE VALVE OUTLET      40.00   1325  10.00   34.00    469    45.500  0.750    1      5.000    7    0.000    -    0.50   45.50
 26  REG.CAT J-BEND          40.00   1325  10.00   34.00    487    44.250  0.500    1      4.625    7    0.000    -    0.50   44.25
 27  ANGLE RISER - L         40.00   1325  10.00   34.00    468    44.000  0.375    1      4.625    7    0.000    -    0.50   44.00
 28  REACTOR RISER - M       40.00   1325  10.00   42.00    492    52.000  0.375    1      4.625    7    0.000    -    0.50   52.00
 29  REACTOR RISER - N       30.00   1025  10.00   50.00    408    61.000  0.500    1      5.000    7    0.000    -    0.50   61.00
 30  REACTOR RISER - P       30.00   1025  10.00   55.00    409    66.000  0.500    1      5.000    7    0.000    -    0.50   66.00
 31  REACTOR RISER - R       30.00   1025  10.00   60.00    410    71.000  0.500    1      5.000    7    0.000    -    0.50   71.00
------------------------------------------------------------------------------------------------------------------
```

```
STRESS PROPERTY VALUES:
==========================================================================================
ITEM  THERMAL  ELASTIC  EQUIV.   EQ.FLD.  INSUL.   EQUIV.  HEAT    EMPTY   TOTAL
CODE  EXPANS.  MODULUS  DENSITY  DENSITY  DENSITY  THICK.  LOSS    WEIGHT  WEIGHT
      IN/FT    PSI*E6   LBS/IN3  LBS/IN3  LBS/IN3  INCHES  BTU/FT  LBS/FT  LBS/FT
----  -------  -------  -------  -------  -------  ------  ------  ------  ------
  1   0.03233   40.55   0.7795   0.0000   0.0000   0.909    73975    5668    5668
  2   0.03414   47.19   0.9035   0.0000   0.0000   1.060    86923    6570    6570
  3   0.03413   45.42   0.8466   0.0000   0.0000   1.123    86910    6778    6778
  4   0.03411   42.66   0.7591   0.0000   0.0000   1.247    80064    6627    6627
  5   0.03409   47.03   0.9018   0.0000   0.0000   1.057    73272    5538    5538
  6   0.01886   31.32   0.5990   0.0000   0.0000   0.772    24444    3227    3227
  7   0.01862   32.54   0.7151   0.0210   0.0000   0.583    20245    2329    8196
  8   0.02844   45.64   1.0308   0.0191   0.0000   0.824    23517    2128    4266
  9   0.03581   40.05   0.7600   0.0000   0.0000   1.168   116007    8917    8917
 10   0.03707   46.43   0.8792   0.0000   0.0000   1.357   122169   10315   10315
 11   0.03707   45.11   0.8366   0.0000   0.0000   1.419   122149   10569   10569
 12   0.03704   43.89   0.7989   0.0000   0.0000   1.480   112456    9971    9971
 13   0.03701   46.27   0.8774   0.0054   0.0000   1.353   102811    8681   13991
 14   0.03700   44.96   0.8352   0.0190   0.0000   1.415   102796    8896   27478
 15   0.04125   41.68   0.7262   0.0133   0.0000   1.310   120398    7687   26269
 16   0.03493   45.21   1.0245   0.0162   0.0000   0.617    27695    1825    3172
 17   0.03476   44.77   1.0179   0.0156   0.0000   0.810    24008    1563    2572
 18   0.03452   44.19   1.0089   0.0145   0.0000   0.801    20318    1341    2028
 19   0.03414   43.33   0.9951   0.0138   0.0000   0.767    16316    1078    1506
 20   0.03351   42.04   0.9731   0.0121   0.0000   0.766    12305     816    1037
 21   0.14428   34.08   0.5525   0.0150   0.0046   0.914     2709     652     872
 22   0.15604   31.03   0.3833   0.0186   0.0046   0.828     2659     414     634
 23   0.15603   30.34   0.3596   0.0188   0.0046   1.078     3006     583     670
 24   0.15562   28.91   0.3116   0.0189   0.0046   3.079     3571    1720    2081
 25   0.03335   37.19   0.7406   0.0035   0.0000   1.016    12325     937    1000
 26   0.03499   41.25   0.9260   0.0036   0.0000   0.751    12935     764     827
 27   0.03508   45.84   1.1427   0.0036   0.0000   0.626    12524     705     766
 28   0.03548   46.85   1.1600   0.0039   0.0000   0.638    15543     847     943
 29   0.02773   43.55   0.3988   0.0040   0.0000   0.791    12569    1135    1275
 30   0.02786   43.89   1.0042   0.0041   0.0000   0.796    13688    1240    1405
 31   0.02796   44.15   1.0085   0.0043   0.0000   0.801    14806    1341    1537
------------------------------------------------------------------------------------------
```

**Computer program calculates** equivalent properties and metal temperatures (Fig. 3).

B31.3.

4. Calculate an equivalent commodity density, ($W_e$), to include the weight of the refractory:

$$W_e = \frac{4\,(W_c\,A_F + \Sigma\,W_{R_i}\,A_{R_i})}{\pi\,d_p^2} \qquad (8)$$

where:

$A_F$ = Internal flow area, sq in.

$A_{R_i}$ = Cross sectional area of refractory layer, sq in.

$W_{R_i}$ = Density of respective refractory layer, lb/cu in.

$W_C$ = Density of fluidized commodity, lb/cu in.

The piping system can now be modeled in the computer using the actual metal thickness, the value $T_s$ for the metal temperature, the value $E_e$ for the modulus of elasticity of the pipe, $W_e$ for the density of the commodity, and the appropriate flexibility factor, k, and stress intensification factors for the miters and bends. Since the pipe diameter, wall thickness, and refractory lining vary within the system, the calculations will have to be repeated a number of times.

A typical transfer line may require as many as 20 sets of calculations in order to be accurately modeled in the flexibility program. Additional calculations are required whenever there is a change in the design, configuration, refractory, etc.

**Computer approach.** A computer program can be written that will perform all these calculations accurately and efficiently. It will store all data and any change could be implemented in minutes.

The piping system is broken down in a number of segments. Each segment with the same physical properties is assigned a code number. Once its properties have been input, the computer would calculate the heat loss, metal temperature, and all the equivalent properties described previously.

The program can be linked to the flexibility program with an automatic or manual transfer of properties. In either case there is a substantial amount of cost and time savings involved, and smaller possibility for error.

An example using Fluor's micro computer program, AUTOTHERM, is shown in Figs. 2-4. The properties of the most commonly used pipe and linings are stored in a library (Fig. 2) for easy access.

Based on given dimensions, ambient conditions, and wind velocity, the program calculates the metal temperature and the equivalent properties (Fig. 3). The program also performs cost energy evaluations by relating BTU loss to dollars (Fig. 4).

**Expansion joints.** In some piping systems, expansion joints must be used to obtain adequate piping flexibility. This is especially true for high-temperature pipe connecting to strain-sensitive equipment such as a gas expander.

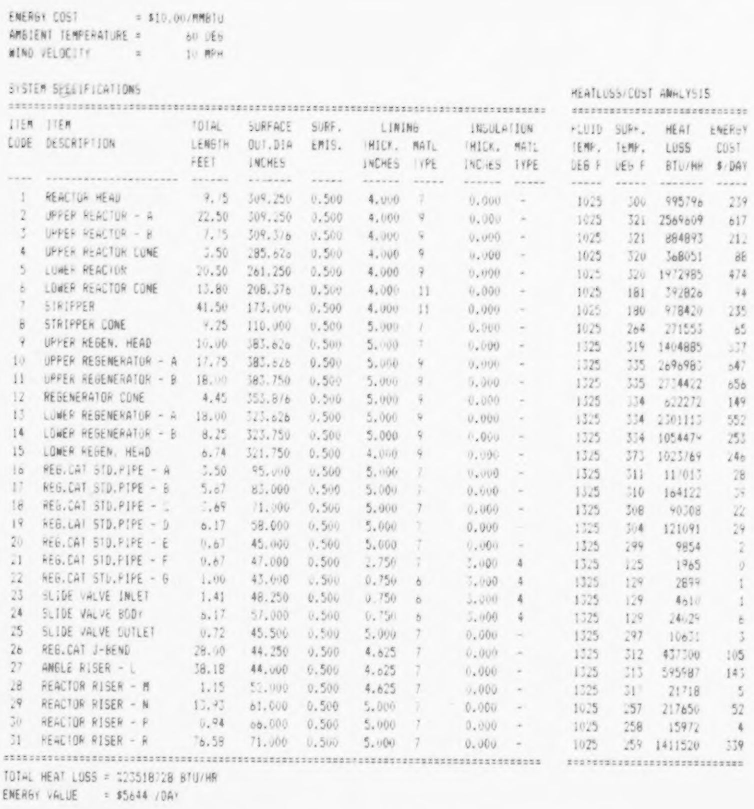
These joints are often highly engineered units that require a considerable amount of attention given to the design and specification details. The stability of the lines in systems using expansion joints is reduced, and generally additional supports and restraints are required.

Extreme caution should be used when selecting and designing expansion joints. Although expansion joints provide an effective method for reducing thermal loads, they provide a weak link in the piping system. They introduce potential pressure-thrust and vibration problems which can cause failures if not considered and accounted for in the design.

**Vibration control.** The flow of catalyst or coke fines through the transfer lines, and the motion of the fluidized beds in the vessels cause surge and impact loads which can induce vibration in the lines. In addition, external seismic and wind loads can cause harmful vibration effects, all of which will cause severe damage to the system if left uncontrolled. The lines must be restrained to minimize vibration, but they must be allowed to move in order to absorb the thermal expansion of the pipe and vessels.

This requires the use of specially designed flexible restraints such as ball-type flexible strut joints and hydraulic snubbers. These restraints must be located and oriented properly to successfully dampen vibration and provide restraint against external loads without interfering with the operation of the system.

Flexible strut joints are usually rec-



```
ENERGY COST          = $10.00/MMBTU
AMBIENT TEMPERATURE =      60 DEG
WIND VELOCITY        =      10 MPH

SYSTEM SPECIFICATIONS                                                                              HEATLOSS/COST ANALYSIS
=================================================================================                 ============================
ITEM  ITEM                    TOTAL   SURFACE  SURF.     LINING        INSULATION                  FLUID  SURF.   HEAT   ENERGY
CODE  DESCRIPTION             LENGTH  OUT.DIA  EMIS.   THICK.  MATL   THICK.  MATL                 TEMP.  TEMP.   LOSS    COST
                              FEET    INCHES           INCHES  TYPE   INCHES  TYPE                 DEG F  DEG F  BTU/HR  $/DAY
----  --------------------   ------  -------  -----   ------  -----  ------  -----                 -----  -----  ------- -----
  1   REACTOR HEAD             9.75  309.250  0.500    4.000   7      0.000   -                    1025    300   995796   239
  2   UPPER REACTOR - A       22.50  309.250  0.500    4.000   9      0.000   -                    1025    321  2569609   617
  3   UPPER REACTOR - B        7.75  309.376  0.500    4.000   9      0.000   -                    1025    321   884893   212
  4   UPPER REACTOR CONE       3.50  285.626  0.500    4.000   9      0.000   -                    1025    320   368051    88
  5   LOWER REACTOR           20.50  261.250  0.500    4.000   9      0.000   -                    1025    320  1972985   474
  6   LOWER REACTOR CONE      13.80  208.376  0.500    4.000  11      0.000   -                    1025    181   392826    94
  7   STRIPPER                41.50  173.000  0.500    4.000  11      0.000   -                    1025    180   978420   235
  8   STRIPPER CONE            9.25  110.000  0.500    5.000   7      0.000   -                    1025    264   271553    65
  9   UPPER REGEN. HEAD       10.00  383.626  0.500    5.000   7      0.000   -                    1325    319  1404885   337
 10   UPPER REGENERATOR - A   17.75  383.626  0.500    5.000   9      0.000   -                    1325    335  2696983   647
 11   UPPER REGENERATOR - B   18.00  383.750  0.500    5.000   9      0.000   -                    1325    335  2734422   656
 12   REGENERATOR CONE         4.45  353.876  0.500    5.000   9      0.000   -                    1325    334   622272   149
 13   LOWER REGENERATOR - A   18.00  323.626  0.500    5.000   9      0.000   -                    1325    334  2301113   552
 14   LOWER REGENERATOR - B    8.25  323.750  0.500    5.000   9      0.000   -                    1325    334  1054474   253
 15   LOWER REGEN. HEAD        6.74  321.750  0.500    4.000   9      0.000   -                    1325    373  1023769   246
 16   REG.CAT STD.PIPE - A     3.50   95.000  0.500    5.000   7      0.000   -                    1325    311   117013    28
 17   REG.CAT STD.PIPE - B     5.67   83.000  0.500    5.000   7      0.000   -                    1325    310   164122    39
 18   REG.CAT STD.PIPE - C     3.69   71.000  0.500    5.000   7      0.000   -                    1325    308    90308    22
 19   REG.CAT STD.PIPE - D     6.17   58.000  0.500    5.000   7      0.000   -                    1325    304   121091    29
 20   REG.CAT STD.PIPE - E     0.67   45.000  0.500    5.000   7      0.000   -                    1325    299     9854     2
 21   REG.CAT STD.PIPE - F     0.67   47.000  0.500    2.750   7      3.000   4                    1325    125     1965     0
 22   REG.CAT STD.PIPE - G     1.00   43.000  0.500    0.750   6      3.000   4                    1325    129     2899     1
 23   SLIDE VALVE INLET        1.41   48.250  0.500    0.750   6      3.000   4                    1325    129     4610     1
 24   SLIDE VALVE BODY         6.17   57.000  0.500    0.750   6      3.000   4                    1325    129    24629     6
 25   SLIDE VALVE OUTLET       0.72   45.500  0.500    5.000   7      0.000   -                    1325    297    10631     3
 26   REG.CAT J-BEND          28.00   44.250  0.500    4.625   7      0.000   -                    1325    312   437300   105
 27   ANGLE RISER - L         38.18   44.000  0.500    4.625   7      0.000   -                    1325    313   595987   143
 28   REACTOR RISER - M        1.15   52.000  0.500    4.625   7      0.000   -                    1325    317    21718     5
 29   REACTOR RISER - N       13.93   61.000  0.500    5.000   7      0.000   -                    1025    257   217650    52
 30   REACTOR RISER - P        0.94   66.000  0.500    5.000   7      0.000   -                    1025    258    15972     4
 31   REACTOR RISER - R       76.58   71.000  0.500    5.000   7      0.000   -                    1025    259  1411520   339
=================================================================================                 ============================
TOTAL HEAT LOSS = 23518728 BTU/HR
ENERGY VALUE    = $5644 /DAY
```

**Cost/energy evaluations** are performed by the computer program (Fig. 4).

## The authors ...

**Malek**

**Tsairides**

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ommended for bracing because they provide tight control against lateral vibration, but allow the pipe to expand axially. They can also allow the line to be braced to the vessel eliminating the need for additional steel structures and the problems associated with vessel nozzle movements.

Where bracing is required against the direction of movement, such as places close to bends and changes in direction, hydraulic snubbers can be used. These devices will allow gradual movement, but will restrain sudden movements that occur during shock loads.

**Design recommendations.** Many problems associated with the design of transfer lines can be avoided if the engineer is careful to evaluate all the conditions which can occur. The following list of recommendations should be considered during the design of these piping systems:

1. Try to avoid hot-wall (externally insulated) designs. However, certain portions of the reactor-regenerator system cannot be cold-wall (internally refractor-lined) designs, in which case, select an optimum ratio between externally insulated and internally lined pipe. This combination can be used to balance the differential thermal expansion between the pipe and vessels and, therefore, reduce thermal loads and stresses. This is especially useful in transfer-line standpipes where erosion is not a problem. Avoid short sections of stainless steel pipe in a refractory-lined system to prevent excessive deformation due to creep, and problems associated with bimetallic welds.

2. Include the elasticity of the vessel shells in the flexibility analysis. This allows for more accurate analysis, and reaction loads can be reduced significantly. Some pipe stress analysis programs will automatically include elastic end conditions for nozzle connections.

When the vessel is refractory lined, an equivalent vessel shell thickness should be used to determine the shell flexibility.

3. Use spring supports or counterweights to help reduce restraint reactions due to dead weight. This is an effective way of providing support without decreasing piping flexibility. However, care must be taken when using these types of supporting devices.

Piping weights must be accurately calculated, and some solid restraints should be included in the design of the support system to minimize line vibration, and to accommodate load variations caused by changes in commodity densities.

4. Take into consideration the stiffness of the structure used to support or restrain the pipe. The structural deflections must be considered along with the loads when designing pipe restraints.

Structural deflections due to wind, seismic, and surge loadings must be included in the analysis of transfer lines.

5. Avoid locating snubbers where there can be a considerable difference in vibration amplitude between the structure and line.

It is preferable that lines be restrained by vessels.

6. Use the microcomputer to calculate heat loss, equivalent pipe properties, and to perform cost/energy studies.

It is a very useful tool for preliminary evaluations, and it provides a systematic documentation of all the piping components and their properties. Data that are required for the analysis of transfer lines is permanently stored and automatically updated as new conditions and components are considered.

**Reference**

1. Turner, W.C. and Malloy, J.F., Thermal Insulation Handbook, Robert E. Krieger-Malabar Florida-McGraw Hill Publishing Companies, New York, 1981.

# How Gaz de France optimizes LNG regasification

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A regasification optimization program was implemented at Montoir-de-Bretagne in 1984, and rapidly accepted by the operators. It has been an important tool for decision-making in the optimizing operation of this liquefied natural gas (LNG) storage and regasification terminal. The models used are regularly and easily updated on the basis of equipment behavior: aging or fouling.

The Montoir-de-Bretagne LNG terminal is in the port area of Nates-Saint Nazaire on the Atlantic coast. It was commissioned in 1982 by Gaz de France.

This terminal is used for receiving, storing, and regasifying the Algerian LNG received under a contract between Gaz de France and Sonatrach, as well as the LNG imported by Belgium and temporarily routed through France.

It is designed to receive 25,000 to 200,000 cu m LNG carriers and has three 120,000 cu m LNG storage tanks. The daily sendout ranges between 6.7 million cu m and 36 million cu m. Montoir terminal supplies mainly Brittany and the Paris area.

Two identical berths (Fig. 1) allow the simultaneous reception of two LNG carriers. LNG is carried to the storage tanks in 32-in. lines at a rate of 12,000 cu m/hr.

Each storage tank is equipped with three submerged 450 cu m/hr pumps with which the LNG is sent from the tanks to the secondary pumps at 8 bar. The nine high-pressure (HP) secondary pumps, with a capacity of either 450 cu m/hr or 180 cu m/hr, raise the LNG pressure to a level at least equal to pipeline pressure prior to revaporization.

The regasification equipment includes:

- Four open-rack seawater vaporizers (ORV) where a total nominal flow rate of 1,800 cu m/hr of LNG is vaporized by 40,000 cu m/hr of water from the Loire River, in countercurrent heat exchangers. When the water temperature is too low, 20 gas-fueled seawater heaters are available.
- An additional seven submerged combustion standby vaporizers (SMV) are able to vaporize approximately 150 cu m/hr of LNG each.

In both cases, the fluid pressure is controlled at about 80 bars. This value was chosen because it is both above transmission pressure and greater than the LNG critical pressure.

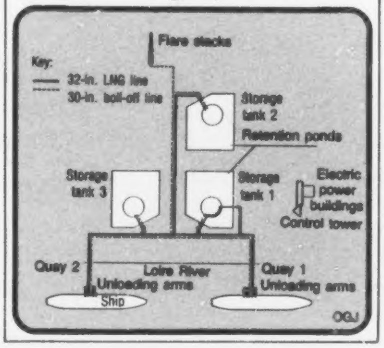
The gas is then metered with high-accuracy equipment and sent into two 36-in. transmission lines. At that point, the gas temperature must be higher than 0° C. to avoid pipeline damage from soil freezing.

The regasification process is efficient and reliable due to the experience of Gaz de France and the quality of the equipment. The main operating principles are:

- The ORVs are base-load equipment. They were designed for nominal sendout and, in most cases, are sufficient for vaporizing the LNG and heating the final natural gas (NG) above 0° C.
- When the Loire River temperature is lower than 6° C., the seawater heaters are successively

Fig. 1

## Unloading system



## Terms used

$T_l$ = LNG inlet temperature
$T_g$ = NG temperature at the outlet of the seawater vaporizers (ORV)
$T_x$ = NG temperature at the outlet of the submerged combustion vaporizers (SMV)
$T_r$ = Required NG outlet temperature
$T_L$ = Loire water temperature
$T_e$ = ORV Water inlet temperature (after a possible heating)
$T_s$ = ORV Water outlet temperature
$T_{bath}$ = SMV bath temperature
D = Total LNG sendout
$D_x$ = LNG flow through an SMV
$D_g$ = LNG flow through an ORV
M = Mass flow rate of seawater to one ORV
$\rho$ = LNG density
$r_1$ = Seawater heater efficiency
$r_e$ = ORV efficiency
$r_x$ = SMV efficiency
$N_g$ = Available number of ORV
$N_x$ max = Available number of SMV
$N_r$ max = Available number of seawater heaters
P = Power required for the regasification of the LNG flow rate
$Q_{water}$ = Heat yielded by the seawater in one vaporizer
$P_r$ = Unit heating rating
$W_r$ = $N_r P_r$ = Total seawater heating rating
$P_x$ = Unit SMV rating
C = Process consumption (MJ/hr of gas). The actual costs can be derived by multiplying C by the price of one MJ of gas.

started up in order to avoid ice formation on the vaporizer tubes. The minimum temperature of the water discharged into the river is approximately +2° C. under nominal flow conditions.

- The stand-by SMVs are basically used for peak-shaving or back-up operation, when an ORV is not available, or when sendout is very high. They also have to be used when the temperature of the gas from the open-rack vaporizers is too low. The temperature of the gas from the submerged combustion vaporizers is about +30° C.

For each operating condition, the operators choose the number of units of each type to be used and the unit operating parameters: water flowrate, LNG flowrate, etc. This choice must not only ensure the wanted NG sendout, but also the proper operation of each unit, and take into account the external parameters such as the Loire River temperature and the desired temperature for the natural gas sent into the grid.

From a strictly technical viewpoint, it is always easy to choose a configuration which allows both nominal sendout and compliance with operating conditions; the facilities are overdimensioned, and operators may generally choose among numerous configuration alternatives. The proper choice must therefore be made on the basis of economics.

In some cases it is fairly simple to reach a decision. When, for instance, the Loire River temperature is high enough to preclude any ice formation and the LNG quantity to regasify is large, only the ORV open-rack vaporizers should be used. ORV operating costs, for the electrical energy used by the water pumps, are far below the cost of the fuel gas which would otherwise be fired in the submerged combustion equipment.

In other cases, however, this issue is more complicated, especially when the Loire River temperature is low. Additional heat is required. The question then is whether the water heaters should be started up and only the open-rack vaporizers used or whether some of the submerged combustion vaporizers should be operated.

Another question may also arise. When the gas sent out or the water discharged into the river is heated unnecessarily due to the configuration chosen, for what period of time may the submerged combustion equipment or the water heaters be shut down while still complying with the minimum temperatures?

Either solution has a major impact on economics. Direct technical LNG regasification costs account for at least 20% of total terminal operating costs which include LNG pump, energy consumption, flared gas, consumables, spare parts, etc. But for a plant of this type, for which considerable design effort was focused on maximizing vaporization efficiency, this percentage could easily be two or three times as large if energy waste was not carefully avoided.

Two examples may highlight this:

- A loss of $19,000/day is incurred when the water discharge into the Loire River is unnecessarily heated by 1° C.
- A loss of $2,900/day is suffered when the gas sendout is unnecessarily heated by 1° C.

As a result of the cost involved as well as the difficulty for the operators to determine the optimum economic configuration, Gaz de France set up a program which enables the operators to solve the following problem at any time: What is the configuration which both minimizes operating costs and complies with equipment operating requirements for given conditions relating to the LNG quantity to regasify, available facilities, and Loire River temperature. The resolution of this problem involved modeling facility performance under constant external conditions and defining the constraints; setting up a stable algorithm for cost minimization; and using it in a minicomputer available at the terminal.

The resulting software is an aid to decision-making. It also provides information on vaporizer throughput as well as on heating costs.

**Optimization program.** The first step in establishing an optimization program consisted of establishing the equations for modeling the behavior of the fluids and of the equipment as well as the performance constraints. First, the function for the costs to be minimized was set up. The equation was determined for the state of the fluids (NG/LNG).

Equations were also established for heat exchange in the open-rack vaporizers, the Loire water heaters, and the submerged combustion vaporizers. Performance constraints were determined for each type of equipment and the overall plant. Some parameters were determined from on-site measurements.

An algorithm was then developed to minimize costs, taking the given constraints into account. It is based on the fact that for a given external set of data, Loire water temperature, sendout rate, temperature of the gas sendout, number of equipment units, etc., only three parameters must be determined: water flow rate in the ORVs, number of SMVs in operation, and LNG flow rate in each SMV.

From these, all other parameters

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Based on a presentation at Gastech 85, Nice, France, Nov. 12-15, 1985.

Table 1

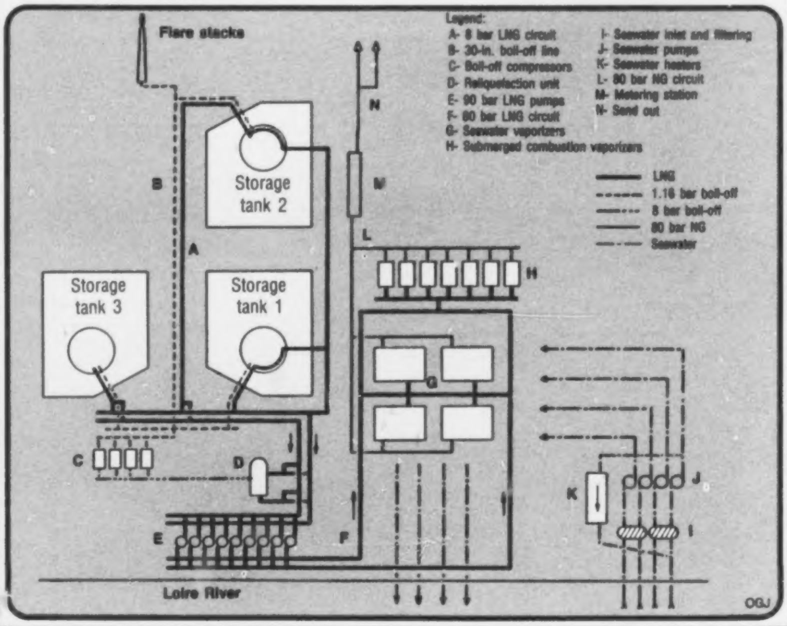
## Regasification of LNG: Computer-aided calculation of an optimal configuration

**Enter (0), or number of the line to be modified:**

| | | |
|---|---|---|
| 1. | Temperature of River Loire water, °C. | 3 |
| 2. | Observed LNG inlet temperature, °C. | -147 |
| 3. | Required NG outlet temperature, °C. | 3 |
| 4. | LNG sendout delivery (cu m/hr) | 300 |
| 5. | Approx. LNG density (kg/cu m) | 460 |
| 6. | Available number of seawater vaporizers | 4 |
| 7. | Available number of seawater pumps | 4 |
| 8. | Available number of autonomous vaporizers | 7 |
| 9. | Available number of seawater heaters | 20 |

Fig. 2

Send-out system


Flare stacks
Legend:
A- 8 bar LNG circuit
B- 30-in. boil-off line
C- Boil-off compressors
D- Reliquefaction unit
E- 90 bar LNG pumps
F- 80 bar LNG circuit
G- Seawater vaporizers
H- Submerged combustion vaporizers
I- Seawater inlet and filtering
J- Seawater pumps
K- Seawater heaters
L- 80 bar NG circuit
M- Metering station
N- Send out
LNG
1.16 bar boil-off
8 bar boil-off
80 bar NG
Seawater
Storage tank 2
Storage tank 3
Storage tank 1
A
B
C
D
E
F
G
H
I
J
K
L
M
N
Loire River
OGJ

involved in the process can be computed.

The algorithm therefore consists in minimizing the cost function while varying these three parameters within their own domain.

**Models and constraints.** The two vaporization methods available have their own specific consumption:

Open rack seawater vaporizers require electric power for the four seawater pumps. The power level is a function of the flow rates, up to 860 kw each.

Heat ouput of the seawater heaters is about 10 mw/heater.

Submerged combustion standby vaporizers have a heat output of approximately 13 mw/vaporizer for the nominal LNG flow rate heated up to +30° C.

These two types of equipment can be put into service together or separately.

The operating consumption (C) for a given configuration can thus be estimated:

$$C = Nx\ Px + Nr\ Pr + f\ (M)\ Ng\ C2/C1 \qquad (1)$$

where:

C = Consumption, MJ/hr

$C_1$ = Cost of a gas kwh, \$U.S.

$C_2$ = Cost of an electric kwh, \$U.S.

$N_x$ = Number of SMV in operation

$N_r$ = Number of seawater heaters in operation

$P_x$ = Unit power of the SMV, MJ/hr

$P_r$ = Unit power of the seawater heaters, MJ/hr

f (M) = Electric power of a water pump in accordance with the mass rate of flow, MJ/hr

$N_g$ = Number of open-rack vaporizers in operation

LNG is regasified at nearly constant pressure, 80 bar. The variations of enthalpy (H) can be used to evaluate the heat flow.

This function was linearized over two temperature ranges:

LNG: $H_l\ (T_l) = h_1\ T_l + h_2$ MJ/ks
Enthalpy of the LNG at 80 bar and $T_l$ (°C.)

NG: $Hg\ (T) = h_3\ T + h_4$ MJ/kg
Enthalpy of the NG at 80 bar and $T_l$ (°C.)

The power (P) necessary for the regasification of LNG at a flow rate of D is:

$$P = \rho D\ [Hg\ (Tf) - H_l\ (T_l)]\ \text{MJ/hr} \qquad (2)$$

where:

$\rho$ = Density of the LNG at $T_l$° C., kg/cu m

D = LNG flow rate, cu m/hr

$T_l$ = LNG inlet temperature, °C.

$T_f$ = NG outlet temperature, °C.

The natural gas outlet temperature is chosen to prevent ice formation on the lines downstream of the pressure regulator, where the expansion may be up to 10 bar. It will thus be close to +5° C.

The four seawater vaporizers are countercurrent heat exchangers in which the LNG flows from bottom to top, while the water runs down around the tubes.

For simplification, the number of vaporizers in operation is considered equal to the number of available vaporizers ($N_g$).

It is very unusual, because of the general operating conditions of the terminal, for the operators to decide to shut down a vaporizer.

The specific heat of water ($C_{water}$) used for revaporization is considered equal to 4.18 kJ/kg °C.

The heat yielded by the water ($Q_{water}$) during the exchange inside a vaporizer is:

$$Q_{water} = MC_{water}\ (Te - Ts)\ \text{MJ/hr} \qquad (3)$$

where:

M = Mass flow rate of water, kg/hr

$C_{water}$ = 0.00418 MJ/kg °C.

$T_e$ = Water inlet temperature, °C.

$T_s$ = Water outlet temperature, °C.

The gas temperature variation and its change of state are calculated as follows:

$$\rho\ Dg\ [Hg\ (Tg) - H_l\ (T_l)] = r_e\ MC_{water}\ (Te - Ts) \qquad (4)$$

Fig. 3

## Vaporization system

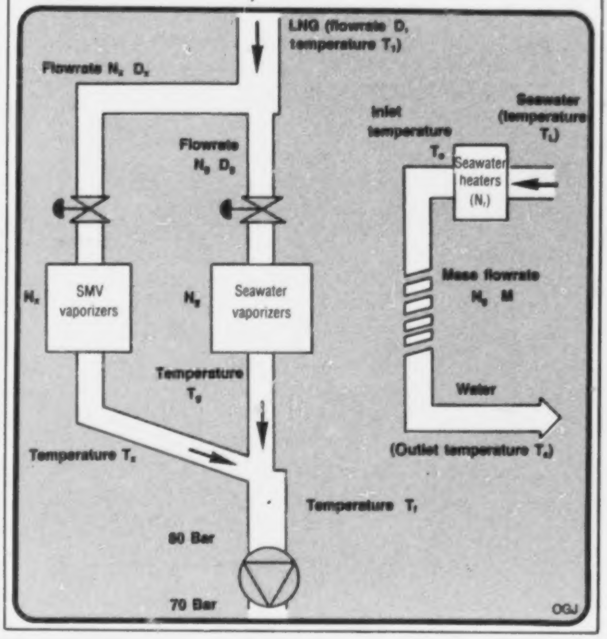

LNG (flowrate D, temperature $T_1$)
Flowrate $N_x$ $D_x$
Flowrate $N_g$ $D_g$
Inlet temperature $T_e$
Seawater (temperature $T_L$)
Seawater heaters ($N_r$)
$N_x$
SMV vaporizers
$N_g$
Seawater vaporizers
Mass flowrate $N_g$ M
Temperature $T_g$
Water
Temperature $T_x$
(Outlet temperature $T_s$)
Temperature $T_f$
80 Bar
70 Bar
OGJ

Fig. 4

## Program procedure

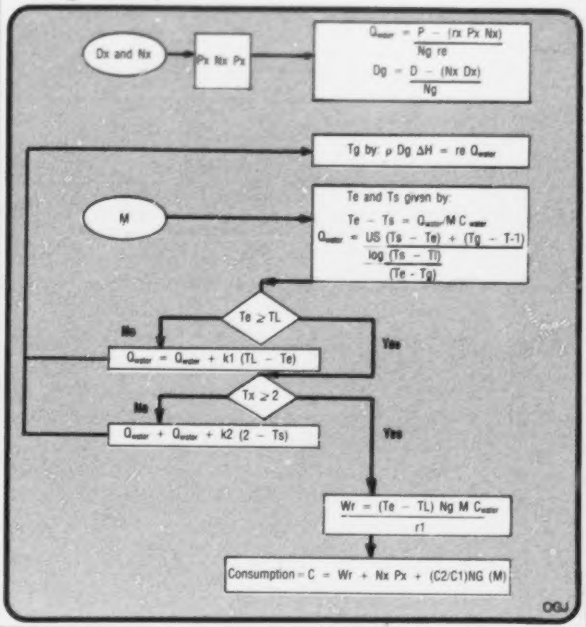

Dx and Nx
Px Nx Px
$Q_{water} = \frac{P - (rx\ Px\ Nx)}{Ng\ re}$
$Dg = \frac{D - (Nx\ Dx)}{Ng}$
Tg by: $\rho$ Dg ΔH = re $Q_{water}$
M
Te and Ts given by:
$Te - Ts = Q_{water}/M\,C_{water}$
$Q_{water} = US \frac{(Ts - Te) + (Tg - T\text{-}1)}{\log\frac{(Ts - Tl)}{(Te - Tg)}}$
Te ≥ TL
No
Yes
$Q_{water} = Q_{water} + k1\ (TL - Te)$
Tx ≥ 2
No
Yes
$Q_{water} + Q_{water} + k2\ (2 - Ts)$
$Wr = \frac{(Te - TL)\ Ng\ M\ C_{water}}{r1}$
Consumption = C = Wr + Nx Px + (C2/C1)NG (M)
OGJ

Table 2

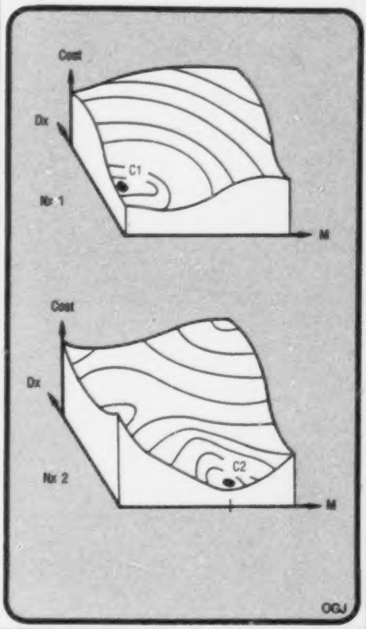
## Results displayed

**Optimal configuration: Corresponding energy cost C = 58261 Mega/J/hr**

| | | |
|---|---|---|
| A. | Number of autonomous vaporizers | 1 |
| | Unit LNG flow rates | < 60 cu m/hr |
| B. | Unit seawater flow rates | < 11754 cu m/hr |
| C. | Number of seawater heaters | 0 |
| | Unit thermic power | 0 Mega J/h |
| D. | Seawater inlet temperature | 3.0° C. |
| | Seawater outlet temperature | 2.0° C. |
| E. | NG outlet temperature (seawater vap.) | 1.7° C. |
| | NG outlet temperature (autonom. vap.) | 35.0° C. |
| F. | NG temperature before discharge | 4.2° C. |

Fig. 5

## Optimization volumes



where:

Dg = Average LNG flow rate in vaporizer, cu m/hr
Tg = Gas temperature at the outlet of the vaporizers, °C.
$T_l$ = LNG temperature at the inlet of the vaporizers, °C.
$r_e$ = Heat exchange efficiency

The heat exchange efficiency is determined experimentally; it represents the influence of various external parameters in the exchange. If re > 1, the LNG receives more heat than is supplied by the water. If re < 1, heat is lost to atmosphere. The geometric characteristics of the exchanger are taken into account in the following equation, especially in coefficient US, which reflects exchange surface and the shape of the tubes:

$$Q_{water} = MC_{water}\ (Te - Ts) = US\ [(Ts - T_l) - (Te - Tg)]/\log[(Ts - T_l)/(Te - Tg)] \quad (5)$$

US and $r_e$ are two independant parameters used to fit the theoretical results to real exchanger behavior: In first approach, sizing calculations, US = Constant = $3.2 \times 10^3$ MJ/hr °C.

Experimentally, US = $MC_{water}$ (Te − Ts) log [(Ts − $T_l$)/(Te − Tg)]/(Ts − $T_l$ − Te + Tg)

Appropriate measurements have shown a linearized function:

US = aDg + b

With a = 0, Dg = LNG flow rate in the vaporizer.

The set of points obtained fit the regression curves quite well, within about 5%. And the derivatives, dUS/dT or dUS/dM, are high in absolute value. So the error inversely made on the predictions is low, about the same order of magnitude as ΔUS dT/dUS, with ΔUS ≈ 5%.

At Montoir, predictions have been possible within 5%. The flow rate (Dg) of LNG through a vaporizer must range between 100 cu m/hr and 550 cu m/hr. The water flow rate (M) to a vaporizer may not be less than $7.5 \times 10^6$ kg/hr in order to ensure correct flow along the tubes. The water outlet temperature (Ts) may not be lower than +2° C. to avoid ice formation in the vaporizers. Water temperature at the vaporizer inlet can be derived from the Loire water temperature:

$$Te = TL + rl\ Pr\ Nr/(Ng\ MC_{water}) \quad (6)$$

Table 3

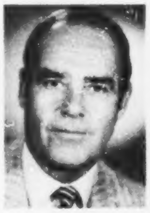
## Configuration comparison

| | Chosen by operators | Recommended by program |
|---|---|---|
| Total water flow rate, cu m/hr | 40,000 | 30,000 |
| Nb of seawater heaters | 0 | 0 |
| Number of SMV | 1 | 1 |
| Unit flow rate, cu m/hr | 140 | 60 |
| Pumping power, kw elect. | 2,800 | 1,700 |
| Heating power | 0 | 0 |
| SMV power, kw gas | 12,000 | 5,200 |
| LNG, sendout rate, cu m/hr | 1,670 | 1,670 |
| Loire River temperature, °C. | 6 | 6 |
| Weighted costs, $/hr | 300 | 150 |
| Potential savings, $/hr | — | 150 |

### The authors. . .

**Colonna**

Jean-Luc Colonna is manager of the technical department, LNG-LPG sector, of the production and transmission division, Gaz de France. He joined Gaz de France in 1974 and has been involved in all technical activities of the company in the field of LNG, including design and operation of LNG receiving terminals, chartering of LNG tankers, and technical assistance for the operation of liquefaction plants. Colonna graduated from the Ecole Polytechnique and Ecole des Mines in Paris.



**Lecomte**

**Caudron**

Bernard Lecomte is general manager of the Montoir-de-Bretagne LNG terminal, Gaz de France. From 1966 until 1970 he was in charge of handling the first French LNG carrier, the Jules Verne. He became plant manager of the LeHavre LNG terminal, and was head project engineer for construction of the 80,000 cu m LNG storage tank at the Fos-sur-Mer LNG terminal.

Stephane Caudron is instrument manager of the Montoir-de-Bretagne LNG terminal of Gaz de France. He graduated in 1982 from the Ecole Polytechnique, and also has a masters degree in automation from the Ecole Superieure d'Electricitie in Paris.

where:

TL = Loire water temperature

Ng = Number of vaporizers in operation (< 4)

Nr = Number of seawater heaters in operation (< 20)

Pr = Unit heater rating, MJ/hr

rl = Water heating efficiency including heat losses

The nominal seawater heater unit rating is 38,000 MJ/hr. It can vary from 25,000 to 45,000 MJ/hr.

The bath temperature in the vaporizers on standby is kept constant at approximately 30° C. through gas combustion, while LNG flows through the vaporizer at a rate Dx.

The relationship between the outlet temperature (Tx) of the gas and the LNG flow rate (Dx) is:

$$Tx = (T_l - T_{bath}) \exp(-A)/(Dx) + T_{bath} \qquad (7)$$

This is based on the heat equation and is adjusted to experimental records by parameter A. This ensures a good correlation between this model and measurements.

The relationship between the heat input (Px) to the SMV and the LNG flow rate (Dx) is given by:

$$Px - \rho\,(Dx/rx)\,[Hg\,(Tx\,(Dx)) - H_l\,(T_l)]\ \text{MJ/hr} \qquad (8)$$

where:

rx = Combustion efficiency, experimentally determined, < 1

The LNG flow rate (Dx) through an SMV must be less than 190 cu m/hr and greater than 60 cu m/hr to ensure stable bath temperature regulation.

For each of the four vaporization water pumps, the manufacturer's diagrams and on-site measurements have corroborated the following empirical polynomial for pump power (Pp):

$$Pp = f(M) = a_2M^2 + a_1M + a_0\ \text{MJ/hr}$$

where:

M = Mass flowrate through one pump, kg/hr

This electric power must be weighted by the ratio of the cost of an electric kwh ($C_2$) to the cost of a gas kwh ($C_1$). The unit flow rate shall not exceed 11,800 cu m/hr: $M < 11.8\ 10^6$ kg/hr. In addition, the flow constraint for the vaporization tubes is: $M > 7.5\ 10^6$ kg/hr.

**Problem formulation.** On the basis of these models and constraints, the problem can be formulated as:

Obtain minimum of

$$[Nx\ Px + Nr\ Pr + (C_2/C_1)\ Ng\ f(M)]$$

With the constraints

$Nx\ Dx + Ng\ Dg = D$

$Ng\ re\ Q_{water} + Nx\ rx\ Px = P$

$Ts > 2°$ C.

$Te > TL$

$Tf >$ chosen value

$M \in (7.5\ 10^6,\ 11.8\ 10^6)$ kg/hr

$Pr \in (25{,}000,\ 45{,}000)$ MJ/hr

$Dx \in (60,\ 190)$ cu m/hr

$Dg \in (100,\ 550)$ cu m/hr

Note that Wr = Nr Pr (total water heating power), Wr is considered as a continuous variable, and Wr ↔ (Nr, Pr) is a bijection.

For a given set of external conditions: TL, $T_l$, Tf, D, and Ng, it is only necessary to know quantities, M, Nx, and Dx, to determine all process parameters (Fig. 4).

The domain described by these three variables is topologically closed and finite. The minimum of the cost function is thus obtained, for external conditions compatible with the constraints, by at least one group of these variables

For each plane (M, Dx, Fig. 5) with Nx determined, a continuous surface is determined, differentiable at almost all points.

A point ($C_1$) will be taken as low as possible on this surface, inside the allowed domain, and the minimal costs thus obtained for each value of Nx will be compared.

The group of three variables eventually chosen will be the one associated with the lowest cost ($C_2$), which will entirely determine the state of the system.

**Program implementation.** The program language is compiled Basic. An Intertechnique minicomputer was chosen for program implementation at Montoir; this system was already used for equipment management applications. This unit has a hard disk capacity of 64 Mbytes, with time sharing on up to 24 consoles.

An operator running the program will enter data as indicated in Table 1.

Nine parameters must be entered by the user. They are sufficient for computing the optimal solution.

The results (Table 2) include an energy cost, C= 58,261 Mega J/hr, which represents the operating costs at the optimal configuration for the conditions given.

**Results.** The savings obtained for given external conditions can be evaluated by comparing actual cases. In one, the implementation of the program would have resulted in daily savings of about $4,000/day (Table 3).

The operators' decision as to the number and type of equipment to use was correct. However, with the Loire water temperature at 6° C., they had chosen the design water flow rate of 40,000 cu m/hr because they feared ice formation in the vaporizers. Without the computer model, they could not know that the water flow rate could be lower without any risk of ice formation.

In another case, using the program would have saved $5,000/day. The operators had chosen to start a submerged combustion vaporizer in order to ensure an adequate NG outlet temperature; it resulted in a higher gas temperature than required. Without the computer model, they could not know that the NG outlet temperature would have been adequate without the vaporizer.

Daily savings would have amounted to $15,000 in a third case. The river temperature was low, so the operators decided to heat the water in order to avoid ice formation in the vaporizer units, and to start up an SMV in order to get an adequate NG outlet temperature, 4° C.

The program suggests that the thermal load of the seawater vaporizers be reduced, and the water flow increased simultaneously, thus preventing ice formation with only a little heating. However, the LNG flow in the SMV had to be increased, which makes the NG outlet temperature rather high, + 14° C.

This configuration proves to be more cost effective than the one chosen by the operators, although the NG is heated too much.

It should be noted that heat input from the water heaters to compensate for the low temperature of the water will have a very limited effect on the NG outlet temperature. In contrast, if the heat required is supplied by the SMV, the NG temperature is considerably increased. This illustrates the advantages of operating the SMV under these conditions.

Recognizing this effect could have produced a potential daily savings of $19,000 in another case. Because the Loire River temperature was very low, 3° C., the operators decided to start up seawater heaters.

Since the LNG flow rate was low, the program recommended establishing a higher water flow rate without any heater, and starting up one SMV, in order to increase the NG outlet temperature.

**Other uses.** An obvious spin-off benefit of the program is that for a given configuration the resulting outlet parameters (temperatures) and the corresponding costs can be predicted. This is a highly appreciated tool.

It should be recalled that the behavior models constituting the heart of the program have been validated experimentally. The program therefore provides excellent quantitative information on the regasification facilities.

Also, model results can be compared to actual measurements after a period of operation. Any impaired correlation between the model and the experimental records is an indication of a quantifiable decline in performance, due to fouling or maladjustment.

The algorithm and the entire program are quite easily transferable to similar plants as well as to different facilities, provided that they take into account different complementary or competitive means of gasification. •

# NELSON COST INDEX

## Refinery construction (1946 basis)

| | 1962 | 1973 | 1983 | 1984 | 1985 | Dec., 1984 | Nov., 1985 | Dec., 1985 |
|---|---|---|---|---|---|---|---|---|
| Pumps, compressors, etc. | 222.5 | 346.9 | 944.5 | 950.5 | 969.9 | 958.4 | 978.3 | 978.3 |
| Electrical machinery | 189.5 | 220.2 | 469.0 | 486.5 | 497.0 | 492.8 | 498.3 | 499.1 |
| Internal-comb. engines | 183.4 | 238.3 | 653.7 | 663.1 | 666.7 | 662.1 | 666.1 | 666.7 |
| Instruments | 214.8 | 338.0 | 675.2 | 696.8 | 713.7 | 701.5 | 721.0 | 725.2 |
| Heat exchangers | 183.6 | 313.7 | 541.7 | 530.9 | 520.0 | 522.8 | 510.4 | 510.2 |
| Misc. equip. average | 198.8 | 291.4 | 656.8 | 665.6 | 673.4 | 667.5 | 674.8 | 675.9 |
| Materials component | 205.9 | 292.3 | 712.4 | 735.3 | 739.6 | 737.4 | 738.5 | 738.7 |
| Labor component | 258.8 | 585.2 | 1,234.8 | 1,278.1 | 1,297.6 | 1,288.6 | 1,296.9 | 1,301.0 |
| Nelson Refinery (Inflation) Index | 237.6 | 468.0 | 1,025.8 | 1,061.0 | 1,074.4 | 1,068.2 | 1,073.5 | 1,076.1 |

## Refinery operating (1956 basis)

| | 1962 | 1973 | 1983 | 1984 | 1985 | Dec., 1984 | Nov., 1985 | Dec., 1985 |
|---|---|---|---|---|---|---|---|---|
| Fuel cost | 100.9 | 186.8 | 913.8 | 968.3 | 878.9 | 959.4 | 816.9 | 823.6 |
| Labor cost | 93.9 | 102.9 | 334.5 | 308.0 | 293.4 | 302.0 | 274.7 | 273.1 |
| Wages | 123.9 | 221.2 | 621.9 | 629.9 | 642.3 | 622.7 | 651.7 | 662.3 |
| Productivity | 131.8 | 214.9 | 186.7 | 204.5 | 219.7 | 206.2 | 237.0 | 242.5 |
| Invest., maint., etc. | 121.7 | 193.0 | 415.3 | 436.6 | 445.8 | 439.6 | 445.4 | 446.5 |
| Chemical costs | 96.7 | 117.3 | 231.3 | 233.4 | 222.9 | 227.1 | 214.2 | 214.0 |
| Nelson operating indexes | | | | | | | | |
| Refinery | 103.7 | 125.7 | 412.9 | 417.4 | 406.8 | 415.0 | 393.1 | 393.6 |
| Process units* | 103.6 | 168.0 | 565.5 | 584.2 | 551.7 | 580.3 | 524.2 | 526.5 |

*Add separate index(es) for chemicals, if any are used. See current Quarterly Costimating, first issue, months of January, April, July, and October.

These indexes are published in the first issue of each month. They are compiled by Gerald L. Farrar, Journal Contributing Editor. An explanation of the indexes is found on p. 145 of OGJ, Dec. 30, 1985.

Indexes of selected individual items of equipment and materials are also published on the Costimating page in the first issue of the month of January, April, July, and October.

# Good operating techniques improve coker yield, increase gas-oil production

**Norman P. Lieberman**
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Metairie, La.

Methods to reduce the production of low-valued sponge coke and increase the volume of hydrocracker and fluid catalytic cracker unit (FCCU) plant feeds are of high interest to refiners. Following are some ideas of the author and representatives of ten major refineries on the subject.

The observations were presented at an experience exchange last May in New Orleans.

**Coke drum temperature.** The hotter the coke drum, the harder the coke. Hard coke means low weight percent volatile combustible matter (VCM).

By keeping a coke drum hot, the 1,000° F. boiling range gas oil is vaporized out of the coke. Heavy gas oil left in the coke thermally degrades to gas, coke, and distillates, or even worse, stays in the coke in the form of VCM.

For every increase of 10° F., the production of heavy gas oil and distillate increases by 1.1 vol % on fresh feed. The proper place to monitor the coke-drum temperatures is in the coke-drum overhead vapor line, upstream of the vapor-line quench injection point.

The beneficial effects of raising the coke drum temperature are greatest at the end of the coking cycle. This is the reason for increasing the coking-heater outlet temperature by 5-10° F. the last 2 hr before switching.

**Steam-out to fractionator.** Using 4,000-5,000 lb/hr of coke-drum quench steam for an hour on a 20,000 b/sd coker, while the drum is still lined-up to the fractionator, may recover an extra 100 b/sd of distillates.

Operators who are abbreviating this "small-steam" step due to fractionator flooding problems or reduced cycles, often count on recovering the residual gas oil and distillates in the coke drum steam-out quench blowdown scrubber.

In practice, this is somewhat of an illusion. The recovered hydrocarbons are partially lost to atmospheric evaporation, or settle to the bottom of water-recovery ponds during the subsequent slop processing. Few coke-drum quench vapor-scrubbing systems operate nearly as efficiently in recovering distillates and gas oil as do coker fractionating towers.

Table 1

## Rules of thumb for delayed cokers

1. Each 8 psi reduction in coke drum pressure reduces coke yield on feed* by 1.0 wt %.
2. Each 8 psi reduction in coke drum pressure increases liquid yields by 1.3 vol % on feed.
3. Each 10° F. increase in coke drum vapor line temperature decreases coke yield by 0.8 % on feed.
4. Each 10° F. increase in coke drum vapor line temperature increases gas and distillate by 1.1 vol % on feed.
5. Each decrease of 1 wt % VCM requires an increase of 7 to 9° F. coke drum vapor line temperature.
6. Reducing recycle by 10% on feed reduces coke yields by 1.2% on feed.
7. Reducing the virgin gas oil content of coker feed by 10% reduces coke yield by 1.5 wt % on feed.
8. Reducing coke yield by 1.0 wt % on feed raises liquid yields by 1.5 vol % on feed.
9. Decreasing cycle time by 6 hr increases coke VCM by 1.0 wt %.

*The term feed refers to fresh resid.

Careful application of distributive computer control has been used to inhibit fractionator flooding and to control the flow of steam during the drum-quench period of the coking cycle. Unfortunately, the number of "not yet completed" computer control projects (none are ever aborted) exceeds the success stories.

**Light distillate recycle.** Employed as a method to enhance coke drum operation over 20 years ago, recycling kerosine and diesel boiling range coker distillate reduces both coke yield and the coke's VCM. For example, the operator of a unit processing 20,000 b/sd of resid, initiated a recycle of 2,500 b/sd of a light distillate and saw the coke make decline by several percent on feed.

**Steam injection.** Most refiners begin injection of steam to the full coke drum prior to completing the switch. Some start the steam flow before breaking down the Wilson-Synder valve.

One delayed coking operator, capacity permitting, uses steam injection to the coke drum during most of the coking cycle. The consequent reduction in the coke drum hydrocarbon partial pressure reportedly reduced coke make enough to pay for the steam consumed ten times over.

**Drum pressure reduction.** The oldest and best known method to minimize coke yield from a barrel of resid is to reduce the coke-drum pressure. Although the May meeting in New Orleans produced no uniformity of opinion on quantifying this (or any other) parameter, the average of the opinions was that:

*Each 8 psi reduction in drum pressure increased liquid yields by 1.3 vol % and cut coke yield by 1 wt % of fresh resid feed.*

It definately appears as if the significance of this correlation has not been related to the first line supervisors operating delayed cokers. Almost 50% of the delayed cokers visited by the author are routinely operating coke drums with partially plugged overhead vapor lines.

The coke-drum overhead vapor lines are cleaned only when the drum operating pressure is starting to approach the relief valve pop pressure. Only when coking capacity is bottlenecked by coke-drum back pressure are the overhead vapor lines "run" (i.e., cleaned with the air operating knockers, turbines, or by hydroblasting) to remove the layered coke deposits inside the vapor lines.

The experience of most operators is that vapor line coke deposits occur principally upstream of the vapor valves; that is, in the section of piping that can be cleaned during the cyclic switching of the coke drums. Some operators clean these overhead lines several times a month.

Often, the decoking crew employed in unheading a coke drum is assigned to "run" the overhead vapor lines during their idle time during the coke cutting portion of the drum cycle.

It is common to see the coke drum pressure drop by 5-8 psi after cleaning. Not only is this an inexpensive method to boost gas oil production, but by maintaining a low pressure

### The author ...

**Lieberman**

Norman Lieberman is a consultant specializing in teaching troubleshooting seminars based on his book, "Troubleshooting Process Operations," PennWell Publishing Co., (Tulsa), 1984, and is working with Trans America Natural Gas on a variety of gas processing projects. Formerly, Lieberman was employed by Amoco Oil (Chicago) as its refinery process coordinator, and as an operating superintendent at Amoco's Texas City refinery.

He is also the author of a variety of articles pertaining to sulfur recovery and alkylation plant operations. Lieberman holds degrees in chemical engineeering from Cooper Union and Purdue University.

difference between the coke drum and the fractionator, the tendency to "foamover" a drum during switching is greatly reduced.

**Recycle ratio.** Refiners who are charging heavy coker gas oil to an FCCU via a cat feed hydrotreater, typically reflux gas oil below the trap-out pan to control ASTM end-point (about 900° F.) and Conradson carbon (not more than 0.2%).

Both of these parameters are a function of the contacting efficiency, as well as the liquid rate across the wash trays.

There is a reasonable probability (although none of the attendees in New Orleans reported doing so) that installation of a structured-type packing wash section below the heavy gas oil trap-out pan would cut the internal reflux rate required to control gas-oil production Concarbon and endpoint. Such a reduction in reflux would, in turn, minimize the coking heater through-put ratio (TPR) where:

$$\text{TPR} = \frac{\text{Coking heater feed}}{\text{Fresh resid feed}}$$

Reducing TPR from 1.20 to 1.10 reduces coke production by approximately 1.2 wt % based on fresh resid feed.

Use of a structured-type packing is quite common in the wash sections of vacuum towers, cracking units, and visbreaker fractionators. Certainly, structured packing has a substantially greater potential to enhance the contacting efficiency within a limited tower vertical space, than do valve trays, bubble cap trays, splash baffles, or show decks.

**Vacuum reduction.** Experiments have shown that reducing the volume of coker fresh feed by 10% through enhanced removal of heavy virgin gas oil in the upstream vacuum tower, will reduce sponge coke yield by 1.5 wt % on fresh resid coker feed. Although, this factor alone respresents big dollar savings, it is only the tip of the iceberg.

More importantly, the thermal degradation of the uncracked virgin gas oil as it passes through the hot coke drum reduces the "K" value, due to dehydration reactions, of the coker gas oil. As the "K" value of gas oil represents, to a great degree, its value as an FCCU feedstock, thermally degrading cat feed in a coker is a significant economic waste.

Several attendees at the New Orleans meeting had implemented, or initiated, projects to enhance vacuum reduction of resid by retrofitting their vacuum systems with ejectors mounted immediately downstream of their vacuum towers. These new ejectors were sized for several thousand pounds per hour of steam, which is designed to be injected in the vacuum heater coils as velocity steam. Use of steam in this manner suppresses temperature peaking in the vacuum heater tubes, as well as reducing the critical hydrocarbon partial pressure in the vacuum tower flash zone.

**Drum insulation.** There are a host of superficially extraneous factors which tend to be overlooked in minimizing coke yields. Some mentioned during the May meeting were:

- Deteriorated coke drum insulation—Water from the coke-cutting operation gets underneath the drum weatherproofing and degrades the insulation integrity. Not only is energy lost, but the cooler drums retain 1,000° F. gas oil in the green coke product.
- Tray flooding due to ammonia sulfide sublimation—High nitrogen content crude oils promote plugging of the tray decks at the top of the coker fractionator with ammonia salts. The trays then flood prematurely with a resulting increase of several psi in back pressure against the coke drum. Periodic, on-stream water washing corrects this problem. Residues produced from the heavy oil extracted from tar sands seem especially susceptible to this problem, possibly due to the nitrogen content of these residues.
- Overhead condenser fin fan external fouling—Coke fines and road dust accumulating around the outside of the cooling fins reduce air flow and heat transfer in the tube bundle. On one unit, this increased the vapor load to the wet gas compressor to such an extent that the compressor suction pressure rose to 8 psig from 3 psig.

The coke drum pressure also increased to 31 psig from 28 psig, with a concurrent and unnecessary escalation in coke yield. This situation was easily corrected by an external, on-stream water wash of the fin-fan tube bundle by the operating crew.

- Slop processing—Depending on how cold refinery slops are preheated and charged to the fractionator, they may induce excessive internal reflux, which in turn increases the TPR, resulting in increased coke and light gas make.

**Beware of shot coke.** The residues from crudes containing a high percentage of asphaltines will tend to form shot coke when processed in a delayed coker. It appears as if successful methods to reduce coke yields (with the probable exception of reduced pressure) will enhance the tendency to produce shot coke.

Minimizing the salt content and the exposure of hot coker feed to oxidation has been suggested as a method to partially inhibit the formation of shot coke. On one, six-drum coker, a clear trend was noticed favoring the formation of sponge coke on the lowest pressure pair of coke drums, while the pair of drums operating at an 8 psi higher pressure (due to a partially coked vapor line) was producing shot coke mixed with sponge coke.

Both sets of drums were charged from a common feed drum with comparable vapor line temperatures.

Table 1 summarizes a few rules-of-thumb for predicting the effect on coking yields of various parameters. While directionally correct, the actual quantitative relationships tabulated should be used with care. • •

## Refining Technology

# Experience improves fluidized-bed combustion

**Iqbal F. Abdulally**
Foster Wheeler Energy Corp.
Livingston, N.J.

**Billy R. Kersey**
Ashland Petroleum Co.
Ashland, Ky.

Table 1

### System operating data

| | |
|---|---|
| 450 psig steam production | 235,000 to 325,000 lb/hr each boiler |
| 150 psig steam production | 15,000 lb/hr each boiler |
| Stack temperature | 350 to 375° F. |
| Calcium utilization | 3 to 5 calcium-to-sulfur molar ratio |
| Combustion chamber temperature | 1,600 to 1,700° F. |
| Bed temperature | 1,525 to 1,575° F. |
| Stack emissions: | |
| Sulfur dioxide | - less than 250 ppm volume* |
| Carbon monoxide | - less than 300 ppm volume* |
| Particulate | - 34 lb/hr per boiler |

* moisture free and oxygen free basis

Operating experience on two fluidized-bed combustion, waste-heat boilers has shown that maximum heat recovery can be obtained from hot, low-heating-value refinery process off gases while maintaining $SO_x$, CO, $NO_x$, and particulate emissions within acceptable limits.

The two units were installed in early 1983 on Ashland's reduced crude conversion (RCC) unit at the Catlettsburg, Ky., refinery. Total operating time, through 1985, has been more than 40,000 hours.

**System description.** Each system consists of a mixing combustion chamber (MCC), a fluidized bed reaction vessel, a steam generator, an economizer, and a baghouse as shown in Figs. 1 and 2.

A high-temperature refinery process flue gas (containing $SO_2$ and CO) and an auxiliary fuel (refinery fuel gas) are burned to generate up to 325,000 lb/hr of 450 psig superheated steam per system. The fluidized bed was included in the system to remove the $SO_2$ from the fluid gases following combustion.

The refinery flue gases are combusted in the refractory-lined MCC at a temperature of approximately 1,600° F. to burn off the CO content of the gases. In addition, the temperature of 1,500 to 1,600° F. is an ideal temperature range for maximum reaction of $SO_x$ with limestone.

Auxiliary fuel and/or excess air is used to control the temperature of the gases exiting the MCC. The gases then enter a refractory-lined reaction vessel containing a fluidized bed of limestone and limestone products.

The fluidized bed is supported on a water-cooled distribution grid plate. The grid plate cools the incoming gases from 1,600° F. to approximately 1,550° F.

These gases then pass through the fluidized bed which captures at least 95% of the $SO_2$ prior to entering the reaction vessel freeboard section. Additional heat may be added to the gases with auxiliary fuel burners as they pass through the freeboard section.

The gases exit to a waste-heat steam generator which generates 650° F., 450-psig superheated steam. Gases exiting the waste-heat steam generator pass through an extended-surface economizer and then to a baghouse for final particulate emissions control.

**Mixing combustion chamber.** The mixing combustion chamber is an 18-ft dia. × 56-ft long, carbon steel, refractory-lined vessel in which the refinery process flue gas and auxiliary fuel gas are mixed with combustion air and burned. The gas inlets, air ports, and burners have been arranged to produce thorough mixing of the air and fuel to maximize combustion prior to exiting the MCC.

**Fluidized bed vessel.** The fluidized-bed reaction vessel is a 46-ft dia. (Fig. 3) × 90-ft high, carbon steel, refractory-lined vessel. The gases enter the vessel through a 15-ft dia. port in the side of the vessel below the grid plate and exit through two rectangular openings on the side of the vessel near the top.

Eight freeboard burners are equally spaced around the circumference of the shell 12 ft above the water-cooled grid plate supporting the fluidized bed.

Fresh sorbent (limestone/dolomite) is fed to the unit through eight, equally spaced nozzles 7 ft above the grid. Normal bed drainage is through two drainage pipes, one on each side of the shell, 4 ft above the grid plate.

**Grid plate.** The water-cooled grid, which supports the bed material, is located about 30 ft above the bottom of the fluidized-bed reaction vessel. It is supported and supplied with water by three vertical, tee-shaped pipe elements. The grid plate is a forced-circulation, water-cooled type. Three vertical pipes enter the reactor shell through the bottom and support three horizontal pipes which form a support structure for the grid plate. The grid plate is of Foster Wheeler construction consisting of closely spaced water-cooled tubes welded to an intermediate fin, to form a continuous airtight panel or structure.

The water circulating within these pipes and the grid plate is part of the low-pressure steam generating system (Fig. 4). The process flue gases pass through fluidizing nozzles which penetrate the fins that join the grid-plate tubes.

**Air and gas flow.** The air and gas flow is shown schematically in Fig. 5. A forced-draft (FD) system was selected because the process flue gases are supplied at a relatively high pressure. Two FD fans provide the total air required to the spent-bed cooler, the seal-air system, the primary and sec-

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Based on a paper presented at the American Petrolem Institute 51st Midyear Refining Meeting, San Diego, May 12-15.

Fig. 1

Side view of system

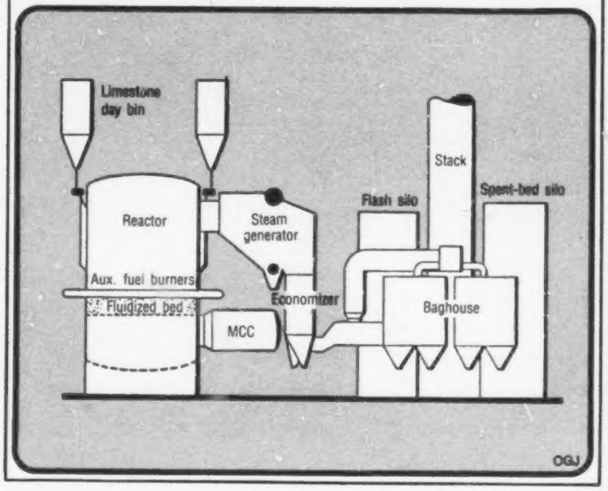
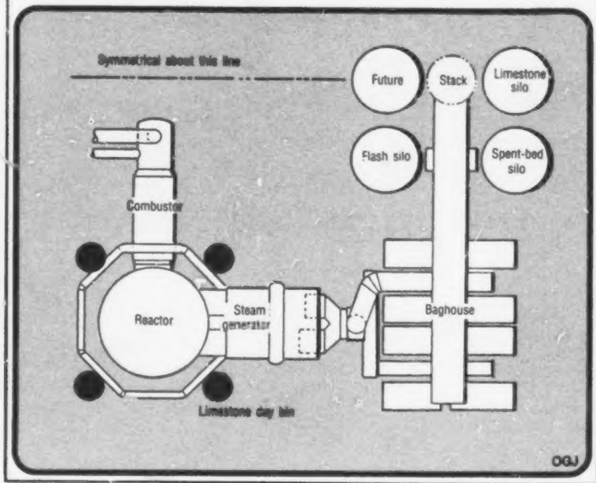

Limestone day bin
Stack
Spent-bed silo
Flash silo
Reactor
Steam generator
Aux. fuel burners
Fluidized bed
Economizer
Baghouse
MCC
OGJ

Fig. 2

Plan view of system


Symmetrical about this line
Future
Stack
Limestone silo
Flash silo
Spent-bed silo
Combustor
Reactor
Steam generator
Baghouse
Limestone day bin
OGJ

ondary/quench air ring headers on the MCC, and the primary air to the freeboard burners via a common manifold header.

The secondary air enters the MCC and mixes with the process flue gases upstream of the auxiliary fuel burners. This mixture flows past the burners where combustion is stabilized.

The eight burners, equally spaced around the circumference of the chamber, burn the auxiliary fuel and are supplied with primary combustion air. Additional air is introduced downstream of the burners to produce additional mixing to ensure complete combustion and to control the bed temperature of the gases exiting the MCC.

The hot gases enter the fluidized-bed reaction vessel, turn 90° in direction, and flow up through a water-cooled distribution grid plate. As the gases pass through the limestone/dolomite sorbent material supported by the grid plate, the $SO_2$ present in the process flue gases is absorbed.

Additional heat may be added to satisfy boiler demand as the gases pass the auxiliary fuel burners located in the freeboard area of the fluidized-bed reaction vessel. The hot gases then pass through the steam generator, economizer, and baghouse prior to exiting through a common stack to the atmosphere.

**Water and steam flow.** Boiler feedwater enters the extended surface economizer, located in the flue, downstream of the steam generator (Fig. 6). This heated water then enters the steam drum which distributes it to the tubes throughout the boiler. The water flows down through the downcomers to the lower drum.

As the water in the boiler bank tubes and the water panels, which form the floor, walls, and roof of the steam generator, absorbs heat from the flue gas flowing past it, steam forms and rises to the steam drum. The water is separated from the steam in the steam drum, and the steam flows out to the drainable superheater where its temperature is raised to 650° F. prior to exiting the steam generator. Fig. 7 is an isometric drawing of the steam generating unit.

**Sorbent feed system.** The sorbent, limestone sized 3,175 μ × 841 μ (⅛ in. × 20 mesh) and dolomite 4,763 μ × 1,191 μ (3/16 in. × 16 mesh), is transported to the two off-site storage silos in covered dump trucks. The sorbent is conveyed from the off-site storage silos via a mechanical belt conveying system to the on-site storage silo (Fig. 8).

The on-site silos consist of precast

Fig. 3

Fluidized-bed reactor details

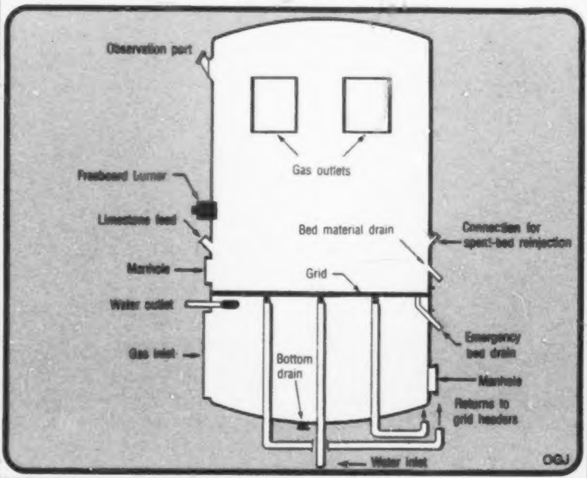

Observation port
Gas outlets
Freeboard burner
Limestone feed
Bed material drain
Connection for spent-bed reinjection
Manhole
Grid
Water outlet
Emergency bed drain
Gas inlet
Bottom drain
Manhole
Returns to grid headers
Water inlet
OGJ

Fig. 4

Grid plate and spent-bed cooling

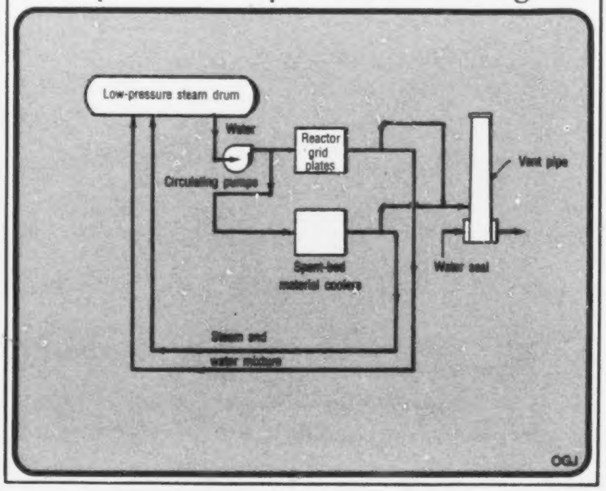

Low-pressure steam drum
Water
Reactor grid plates
Vent pipe
Circulating pumps
Spent-bed material coolers
Water seal
Steam and water mixture
OGJ

Fig. 5

Air and gas flow schematic

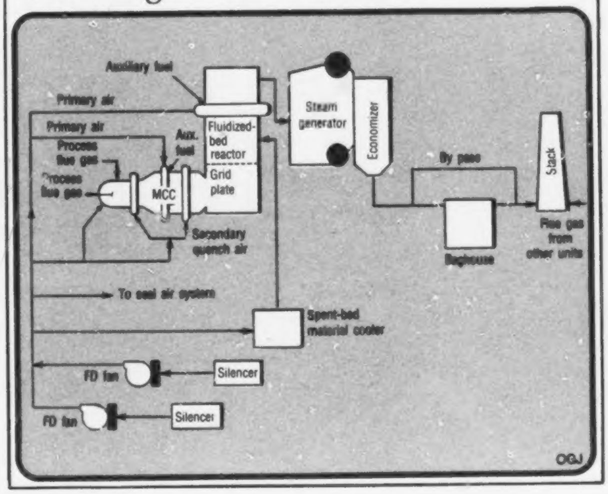
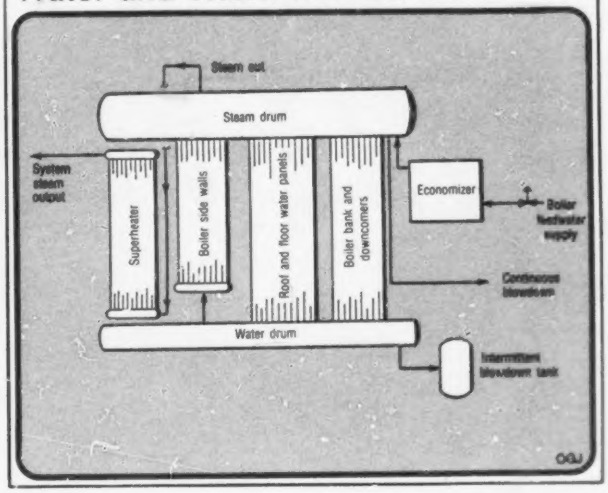

Auxiliary fuel
Primary air
Primary air
Process flue gas
Process flue gas
Aux. fuel
MCC
Fluidized-bed reactor
Grid plate
Secondary quench air
Steam generator
Economizer
By pass
Stack
Baghouse
Flue gas from other units
To seal air system
Spent-bed material cooler
FD fan
Silencer
FD fan
Silencer
OGJ

Fig. 6

Water and steam flow schematic


Steam out
Steam drum
System steam output
Superheater
Boiler side walls
Roof and floor water panels
Boiler bank and downcomers
Economizer
Boiler feedwater supply
Continuous blowdown
Water drum
Intermittent blowdown tank
OGJ

concrete stave silos supported on a cast-in-place concrete base. Sorbent from the on-site silo passes through bin activators and is pneumatically conveyed to four day bins located above each fluidized bed reaction vessel (Fig. 1).

The day bins are 12-ft diameter × 36-ft high carbon steel vessels. The sorbent passes thorugh a screw conveyor and rotary airlock prior to falling by gravity to the fluidized bed.

A low level indicator in the on-site storage silo, and each of the bins, will automatically initiate operation of the system for refilling. The on-site silo and bins hold a 1½-day supply of sorbent with full load operation. The sorbent feed into the fluidized bed reaction vessel is controlled to maintain $SO_2$ emissons at the stack within limits.

**Bed material removal.** Bed material is discharged from the fluidized-bed reaction vessel through an overflow weir into a spent-bed cooler (Fig. 9). In the spent-bed cooler, the spent-bed material is fluidized and partially cooled by air fed from the FD fan. The heated air is routed from the spent-bed cooler to the freeboard of the fluidized-bed reaction vessel.

Additional heat is extracted from the spent-bed material via cooling coils. The water flowing through these coils is part of the low-pressure steam generating system. The bed material is cooled from 1,600° F. to approximately 335° F. by the combined cooling of air and water.

The spent-bed material is discharged from the spent-bed cooler through an overflow weir into a surge hopper and then pneumatically conveyed to an on-site storage silo. The on-site storage silo holds in excess of a 1-day supply of spent-bed material. The spent-bed material is then pneumatically conveyed to the offsite storage silo for removal by truck.

**Fly ash removal.** Fly ash drops out of the flue gas and is collected in hoppers located below the steam generator and the economizer (Fig. 10).

The fly ash collected in the steam generator hopper falls by gravity into the economizer hoppers.

The fly ash collected in the economizer hoppers is removed by two screw-type conveyors and discharged into a pneumatic conveying system. The flue gas exiting the economizer passes through a baghouse, before it is released up the stack to the atmosphere. The fly ash collected in the baghouse hoppers is also removed by screw conveyors, discharged into a pneumatic conveying system, then conveyed to an on-site storage silo

Fig. 7

Steam generating unit

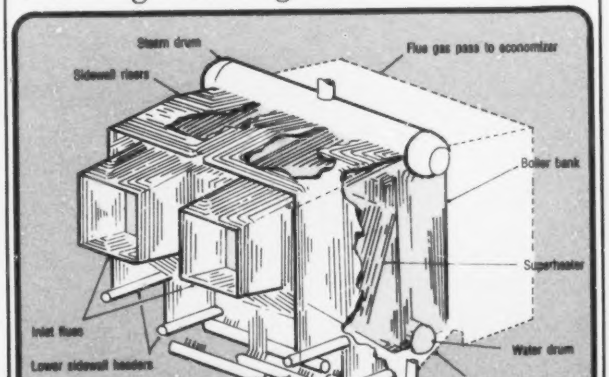

Steam drum
Flue gas pass to economizer
Sidewall risers
Boiler bank
Superheater
Inlet flues
Lower sidewall headers
Water drum
Fly ash hoppers
Superheater headers
Superheater feeder
OGJ

Fig. 8

Limestone/dolomite handling system

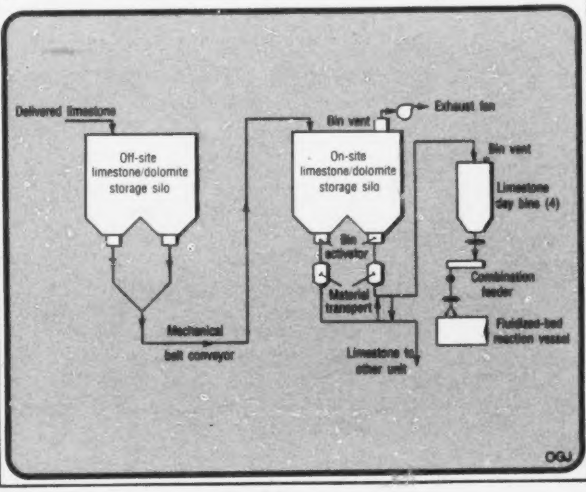

Delivered limestone
Off-site limestone/dolomite storage silo
Mechanical belt conveyor
Bin vent
Exhaust fan
On-site limestone/dolomite storage silo
Bin vent
Limestone day bins (4)
Bin activator
Material transport
Combination feeder
Fluidized-bed reaction vessel
Limestone to other unit
OGJ

Fig. 9

## Bed material removal system

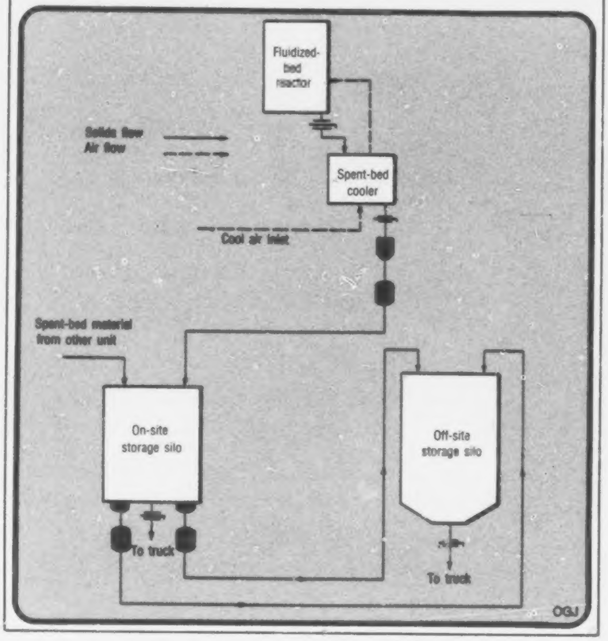
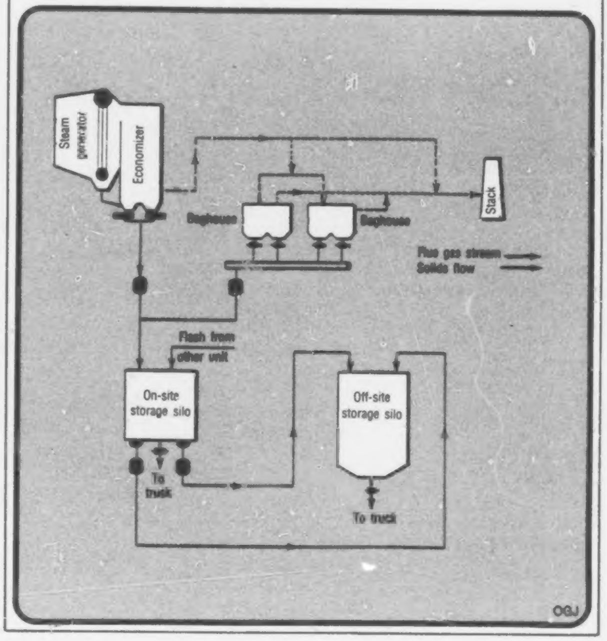


Fig. 10

## Flash removal system



which holds in excess of a 1-day supply of fly ash. The fly ash is then pneumatically conveyed to the off-site storage silo for removal by truck.

**Considerations.** In the planning stages for the reduced crude conversion (RCC) unit, Ashland engineers recognized that the waste flue gases would require special consideration. Environmental concerns dictated the recovery of 95% of the design $SO_2$ and $SO_3$ before they could be exhausted to atmosphere.

The control of CO and particulate emissions was equally important but not considered to be as difficult to achieve. Economics dictate that the sensible heat and the heat of combustion should be recovered.

The initial design concept envisioned a conventional CO boiler followed by a caustic scrubber. The latter would remove the $SO_x$ and the particulates, and was the only known system which was capable of the required level of $SO_x$ reduction. The ideal of firing a fluidized-bed boiler with a gaseous fuel evolved more slowly. A caustic scrubber had been proven in fluid catalytic cracking (FCC) process-waste-flue-gas service and was, at that time, considered the best state-of-the-art. However, the disadvantages were numerous. In addition to the high cost of caustic, they included the following:

- The scrubber would remove the $SO_2$ in the form of soluble sodium sulfite. The effluent would require further treatment by reaction with lime in clarifiers to form calcium sulfate. In order for this material to be suitable for landfill, it would need to be oxidized to the calcium sulfate form by blowing with air. Vacuum filters would probably be required to prepare the wet sludge for the landfill.
- The conventional CO boiler, as used by many refineries for FCC units, normally has a casing design pressure of 20 in. of water. Since the boiler would be upstream of the caustic scrubber, fans would be required to compress the entire volume of RCC flue gas and combustion air to the pressure required by the scrubber.
- The boiler/economizer unit would have to be designed for fairly high exit gas temperature to minimize corrosion because of the high $SO_x$ level.
- Reheat would probably be required before the scrubber exhaust gas could be discharged to atmosphere.
- The landfill of a wet sludge could be troublesome.

Ashland engineers were aware that an atmospheric fluidized limestone bed boiler system had been developed for the combustion of coal and the capture of the $SO_x$ formed. Also some conceptual work was being done for pressurized fluidized bed boilers so that the hot exhaust gases could drive power expansion turbines.

Ashland's concepts for a pressurized fluidized bed boiler to combust and desulfurize hot gases evolved from this knowledge. It became apparent that this design would have several advantages. They would include the following:

- The RCC flue gas could remain pressurized through the entire train. This would reduce power requirements drastically as the only fans required would be for combustion and quench air.
- The raw material would be locally plentiful and relatively cheap limestone and dolomite.
- The boiler/economizer unit could be designed for a low exit temperature, since the $SO_x$ would be minimal at that point.
- The stack gases would be dry and no reheat would be required.
- The fly ash could be removed by a conventional baghouse.
- The spent-bed material and fly ash would be a dry, nonhazardous material suitable for landfill disposal.
- The relatively low combustion temperature of about 1,650° F. would minimize the formation of additional $NO_x$.

A pilot plant test program was funded by Ashland Petroleum Co. and conducted by Foster Wheeler to determine the feasibility of the fluidized-bed boiler application developed by Foster Wheeler. The test results were encouraging, and the decision was made by Ashland management to proceed with the construction of the boilers.

**Operating experience.** The two boilers were first started up in February and March of 1983. The total operating time through 1985 has been more than 40,000 hours. Downtime

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includes shutdowns for routine inspections, maintenance on auxiliary equipment and boilers, and operations reasons such as reduced steam demand by the refinery complex.

The primary goals of the project, which were the control of $SO_2$ and CO emissions and the recovery of heat, have been met. The sorbent-utilization rate is satisfactory, and sulfur capture is better than 95%. The sorbent used is normally a blend of limestone and dolomite. The feed of 100% limestone shows no improvement over the use of the limestone-dolomite blend.

**Operating data.** The waste heat boiler produced 450 psi, 650° F. steam for use in condensing steam turbines. The water-cooled support grid for the bed produced 150 psig saturated steam for general refinery use.

The efficiency on a lower-heating-value basis is about 80%. This compares favorably with CO boilers in more conventional refinery operations. Table 1 gives the operating data of the units. ▪

# One-step process takes $H_2S$ from gas stream

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**A** novel, one-step process selectively removes hydrogen sulfide from sour gases and converts dissolved hydrogen sulfide directly to sulfur in a bubble tower filled with a sweetener solution.[1]

The sweetener is a proprietary formulation consisting of an alkaline solution of oxidizing and buffering agents. Oxidation of hydrogen sulfide to sulfur is achieved by a liquid-phase oxidation technique.

Various sour gas sweetening processes have been used for a number of years. Incentives for use of the one-step process include:

1. Improved economics for hydrogen sulfide removal based on cost-performance evaluations
2. Simplicity of operation
3. Low capital cost requirements for the gas processing plant
4. Adaptability to existing process equipment
5. Low toxicity and nonhazardous waste characteristics of the spent slurry generated by the hydrogen sulfide reaction.

This article presents the current understanding of hydrogen sulfide oxidation chemistry in nitrite solutions, as well as research and field data related to the one-step process.

The field data provide quantifiable proof that the one-step process is a viable economical alternative for hydrogen sulfide removal in properly designed and operated equipment.

## Chemistry

Hydrogen sulfide ($H_2S$) is commonly encountered in a concentration range of a few ppm to about 15% in process gas streams during oil and gas production.

Its high toxicity (threshold limit value = 10 ppm/8-hr average; inhalation $LC_{50}$ = 444 ppm/4 hr) and corrosivity dictate the need for its complete removal from sour gas streams.

A brief overview of the chemistry used in the design of several available technologies for sweetening sour gas was previously presented.[2]

The one-step process is a batch process for absorbing $H_2S$ from sour gas bubbled through a proprietary formulation of nitrite ions in a bubble tower.

The dissolved $H_2S$ is then oxidized to sulfur by nitrite ions:

$$3H_2S + NO_2^- \rightarrow NH_3 + 3S + OH^- + H_2O$$

Some recently completed studies indicate that this liquid-phase oxidation of dissolved $H_2S$ is an autocatalytic reaction with an induction period.[3] These observations are similar to those reported in the literature.[4-11]

The oxidizing agents used in other research were oxygen, hydrogen peroxide, sulfite ions, nitrous acid, etc. Some additional conclusions reported in the recent studies are presented in Table 1.

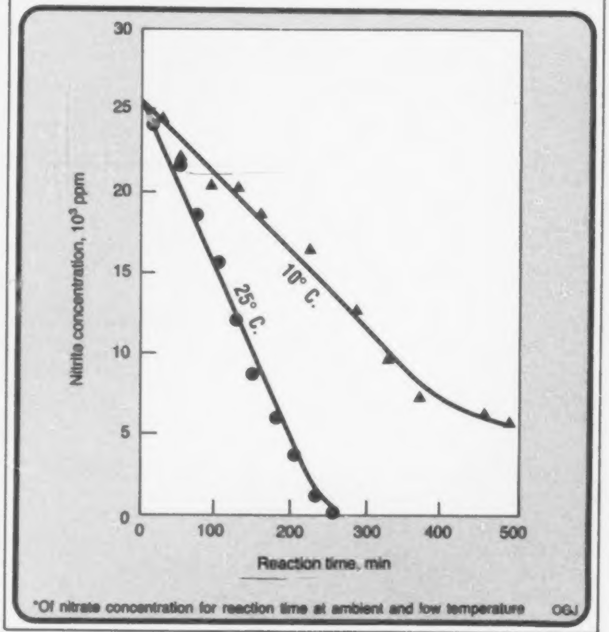
Based on a study of reaction mechanism and kinetics, the mechanism given in Table 2 was proposed.

At the start of the oxidation of dissolved $H_2S$ with oxygen, hydrogen peroxide, and sulfite ions, there is an induction period, suggesting autocatalysis, i.e., a reaction product accelerates the reaction.

Based on a paper presented at the Spring Meeting of AIChE in New Orleans, April 6-10, 1986.

Fig. 1

Profile comparison*



*Of nitrate concentration for reaction time at ambient and low temperature

OGJ

Fig. 2

Typical $H_2S$ scrubber

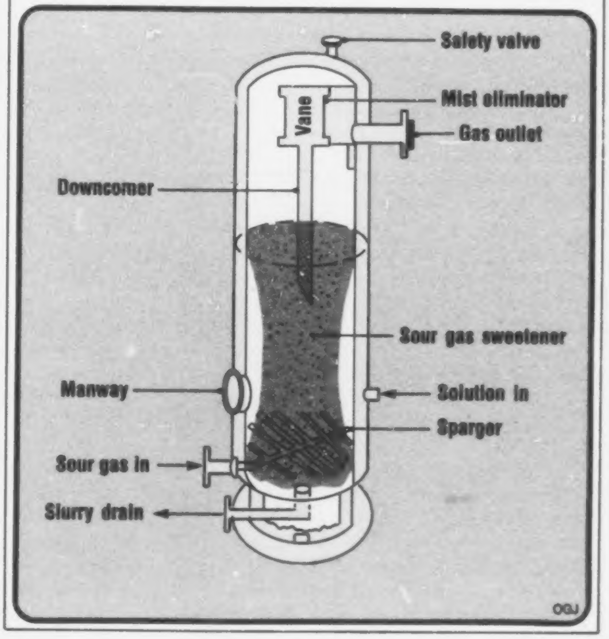


Table 1

## Liquid-phase oxidation*

1. The oxidation of hydrosulfide ions ($HS^-$) with nitrite ions is independent of nitrite concentration between 0-25,000 ppm $NO_2^-$.
2. The rate constants for nitrite depletion at pH 7.9 and at 10° C. (50° F.) and 25° C. (77° F.) are $1 \times 10^{-3}$ and $2.6 \times 10^{-3}$ mole/l./min respectively (Fig. 1). The rate constant doubles for every 10° C. (18° F.) rise in temperature.
3. The activation energy based on the rate of nitrite depletion is 10.45 kg-cal/mole.
4. The rate constants are pH-dependent.
5. Polysulfides are most probably formed as intermediates.
6. Ammonia is the main product of nitrite reduction.
7. There is a net production of hydroxide ion during the reaction.

* Conclusion of a study of $H_2S$ with nitrite ions.

Table 2

## Reaction mechanism*

1. Dissolution and dissociation: $H_2S$ (gas) $\leftrightarrows$ $H_2S$ (aqueous) $\leftrightarrows$
   $H^+ + HS^-$; $pK_{a1} = 7.02$
   $HS^- \leftrightarrows H^{++} S^{--}$ $pK_{a2} = 12.35$ to $15.0$
2. Oxidation:
   $2HS^- \leftrightarrows S_2^{--} + 2H^{++} 2e^-$ (Rate determining)
   $S_x^{--} + Hs^- \leftrightarrows S_{x+1}^{--} + H^+ + 2e^-$
3. Reduction:
   $NO_2^- + 5H^+ + 6e^- \rightarrow$ $NH_3 + 2OH^-$
4. Sulfur formation:
   $S_{x+1}^{--} \leftrightarrows$ S (aqueous) $+ S_x^{--}$
   $H^+ + S_2^{--} \leftrightarrows$ S (aqueous) $+ HS^-$

*The auto-oxidation of hydrosulfide ($HS^-$) is the rate-limiting step because the electrostatic repulsion between two anions makes close approach difficult. The subsequent oxidation steps involving polysulfides are thought to be faster because of their delocalized () electron system.

Polysulfide ions are postulated as catalysts in these reactions. The rate of reaction is independent of concentrations of the oxidizing agent.

In the liquid-phase oxidation of $H_2S$ with nitrite ions, the addition of synthetic polysulfide ions did not eliminate the induction period. A derivative of polysulfide ions or a metal chelate eliminated the induction period.

These observations suggest that in the liquid-phase oxidation of hydrogen sulfide with nitrite ions, the catalyst is other than polysulfide ions.

The one-step process employs the latest available knowledge to eliminate the induction period and make it a trouble-free, simple operation.

**Process application.** The one-step process is normally run in a vertical bubble tower (Fig. 2), and is most suited for sweetening sour synthetic, natural, and associated gas containing 1 ppm to about 1% $H_2S$. Recently, on an offshore drilling ship, the one-step process was used to sweeten sour gas containing about 5% $H_2S$.

Although there are no chemical limits for the maximum $H_2S$ concentration which can be removed with the oxidizing solution used in this process, economics in terms of the required equipment and operating costs will generally dictate a choice between the one-step or alternate processes.

It is important to keep the pH above 7.5 to control selectivity and to optimize efficiency of $H_2S$ removal with this buffered oxidizer.

One gallon of this specific oxidizer removes in excess of 2 lb of $H_2S$ when the gas entering the bubble tower is at ambient temperatures (below 45° C.).

If the gas temperature exceeds 45° C., then the efficiency of $H_2S$ removal with this particular oxidizing solution may not conform to the empirical relationship; partly because the solubility of $H_2S$ in aqueous alkaline solutions is lower at temperatures above 45° C.

Proper equipment design must include close attention to a number of variables based on established empirical factors and sound engineering principles.

Important to a proper unit design is to size a vessel that satisfies four critical criteria related to vessel pressure rating, i.e., minimum acceptable di-

Fig. 3

## Contact time requirement

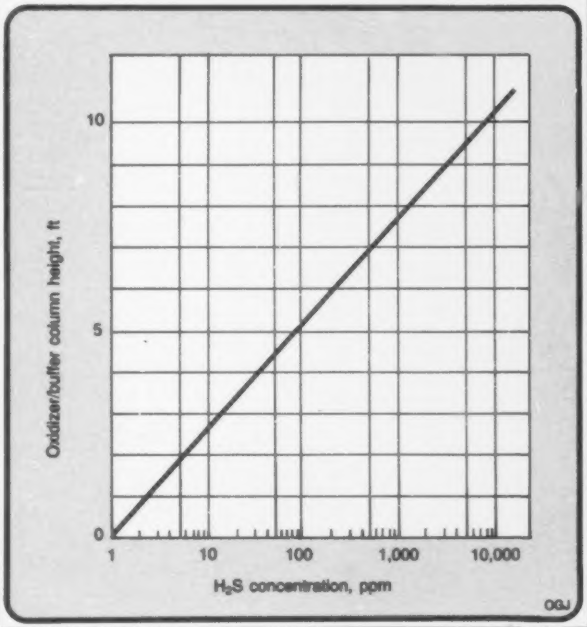
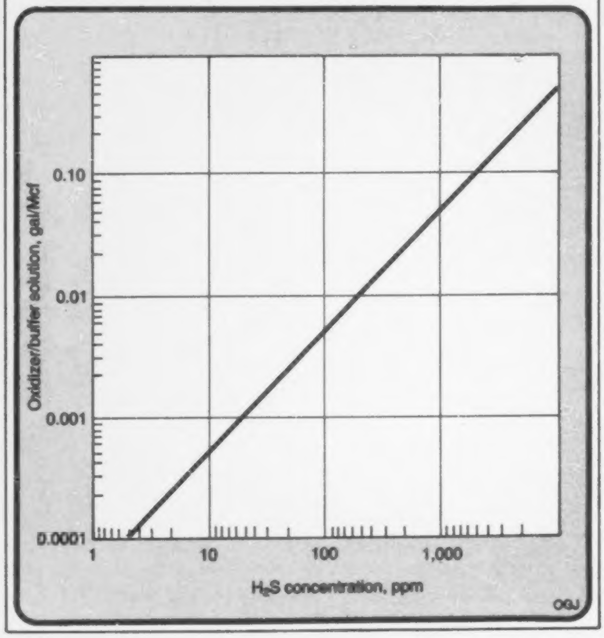


Fig. 4

## Oxidizer/buffer requirement



ameter, oxidizier solution column height, and solution capacity of the vessel.

The calculation of vessel dimensions can be readily made based on the following information for the sour gas:

- Gas flow rates to be processed
- Hydrogen sulfide concentration to be removed
- Gas pressure
- Gas temperature

**Equipment design guidelines.** A gas plant for the one-step process can be designed using the above-stated sour gas data, known engineering principles,[12] and empirical relationships.

These empirical relationships are based on experiences gained in field applications and studies conducted in a pilot unit.

A minimum operating pressure, approximately 20 psig, is required for proper unit performance.

Stable operating conditions are difficult to achieve below 20 psig because feed gas pressures normally fluctuate by several psig. A minimum of 35 psig provides a reasonable margin of safety.

The one-step process can be operated at any pressure higher than 20 psig so long as the feed gas is not liquefied under pressure, and passing of the compressed gas through the aqueous solution will not create conditions for ice formation.

The vessel diameter for the $H_2S$ scrubbing tower should produce a homogeneous bubble flow.

The selection of vessel diameter is made based on known engineering principles.

The homogeneous bubbling flow is necessary to produce an intimate mixing of gas and liquid without creating conditions that contribute to the carryover of the oxidizing solution into the effluent gas line.

The gas-to-liquid contact time needed for selective removal of $H_2S$ using the specified oxidizer solution can be selected based on the empirical relationship shown in Fig. 3.

With a given volume of oxidizer solution in the vessel, the run period can be estimated from an empirical relationship.

Oxidizer solution required:

$$\text{gpd} = 0.0473 \times \text{MMscfd} \times \text{ppm}$$

where ppm = $H_2S$ concentration, v/v

The general considerations given here are applicable in most instances.

**Field data.** The one-step process is being used successfully in 12 states with more than 80 units in operation at this time.

Table 3

## System applications

| Gas properties | Gas processing plant A | B | C |
|---|---|---|---|
| Flow rate, Mscfd | 200-400 | 2,000-4,000 | 4,000 |
| $H_2S$ (in), ppm | 1,400-2,000 | 250-500 | 200 |
| $H_2S$ (out), ppm | 0 | 0 | 0 |
| $CO_2$ (in), % | 6-8 | 0.2-0.3 | 3 |
| $CO_2$ (out), % | 6-8 | 0.2-0.3 | 3 |
| Pressure, psig | 35 | 250 | 850 |
| Temperature, °C. | <40 | <40 | <45 |
| **Operating system** | | | |
| Tower dimensions, ft | 4 × 28 | 7 × 20 | 4 × 24 |
| Pressure rating, psig | 100 | 275 | 1,400 |
| Inlet and outlet gas pipe diameter, in. | 6 | 6 | 4 |
| Oxidizer solution requirement, gal/run period in days | 530/35 | 2,500/77 | 1,100/29 |
| Oxidizer solution column height, ft | 9 | 9 | 12 |

Table 4

## Spent slurry composition*

| Parameter | Liquid | Solid |
|---|---|---|
| Water, wt % | 36.7 | |
| Nitrite, wt % | 1.0 | |
| Nitrate, wt % | 0.9 | |
| Bicarbonate, wt % | 8.2 | |
| Carbonate, wt % | 1.2 | |
| Sulfate, wt % | 1.7 | |
| Tetrathionate, wt % | 2.5 | |
| Ammonium, wt % | 0.3 | |
| Sodium, wt % | 7.3 | |
| Sulfur, wt % | | 20.2 |
| Sodium bicarbonate, wt % | | 17.7 |
| Sodium sulfate, wt % | | 0.7 |
| Sodium tetrathionate, wt % | | 1.6 |
| Total, wt % | 59.8 | 40.2 |

*The typical slurry has a pH of 8.0 and does not contain heavy metals, cyanides, sulfides, or chlorinated organic compounds.

The operating units in California are both onshore and offshore.

One unit is operating on a North Sea platform.

Several units are under construction for use in Canada.

These installations include use of equipment designed to the recommended specifications as well as modifications of existing equipment.

Three case histories (Table 3) illustrate some of the successful operations.

A gas-processing plant (A) operated by a major oil company in California collects gas from a steamflooded field and processes between 200-400 Mscfd gas containing 1,400-2,000 ppm $H_2S$.

The gas plant is located in a residential area containing a park and school. Leakage of $H_2S$ or oxides of sulfur into the atmosphere is not permitted.

Prior to switching to the one-step process, zinc compounds were used for $H_2S$ removal, but the method using zinc compounds was discontinued because the spent slurry was classified as toxic and hazardous.

The second gas plant (B) operator also utilized existing equipment with minor modifications to switch to the one-step process about 1 year ago.

This plant is located in a rural area of West Texas.

It processes between 2 and 4 MMscfd gas containing 250 to 500 ppm $H_2S$ depending upon the number of wells being produced.

The run period of about 77 days is obtained when an average of 2.5 MMscfd gas containing 275 ppm $H_2S$ is processed through a column of 2,500 gal of oxidizer solution.

The spent slurry is disposed of by spreading on farm land.

The third gas plant (C) is located in a rural area in Kansas.

This plant processes 4 MMscfd gas containing 200 ppm $H_2S$ at 850 psi and 31° C.

A heater is provided to heat the gas to a temperature between 25 and 44° C. whenever the gas temperature drops below 20° C.

The original equipment, a 4 ft × 24 ft tower, was designed to operate with a metal oxide compound, but it was modified in order to operate with the oxidizer solution.

A run period of 29 days is normally achieved with 1,100 gal of the oxidizer solution.

The spent slurry is disposed of by spreading on farm land.

**Costs and benefits.** The data collected in the field applications were used to derive an empirical relationship (Fig. 4) which relates to the consumption of oxidizer solution by $H_2S$ present in 1,000 cu ft of gas.

For $H_2S$ concentration between 10 and 100 ppm, the chemical consumption cost to process 1,000 cu ft of gas would range from a fraction of a penny to less than 10% of the sale price of the processed gas.

A cost performance evaluation indicates that the one-step process is very attractive where $H_2S$ concentrations are 1% or lower, low capital investment for equipment is desired, and low operating costs are required.

An added benefit is the substantial cost savings on waste disposal, e.g., the spent slurry of sulfur and sodium salts is classified as a nonhazardous waste by a number of regulatory agencies.

The disposal cost for nonhazardous waste is 20-25% of the disposal cost for hazardous waste produced by the users of iron and zinc compounds, caustic soda, and formaldehyde.

## Environmental considerations

The batch processes based on the use of formaldehyde, zinc compounds, iron sponge, or caustic soda remove $H_2S$ from sour gas and convert it to sulfide.

Formaldehyde produces polymeric organic sulfides and mercaptans, zinc and iron produce corresponding heavy metal sulfides, and caustic soda produces sodium sulfide.

Since by-product waste from all of these processes contains sulfides, heavy metal, or both, waste disposal is costly and difficult.

These wastes are generally classified as hazardous because of their heavy metal and sulfide content. They also present operating problems and difficulties related to handling hazardous material and waste.

For example, $H_2S$-saturated iron sponge is pyrophoric and will release $H_2S$ back to the atmosphere under certain conditions.

A number of regenerative processes based on multivessel designs also use the liquid-phase oxidation technique to oxidize $H_2S$ to sulfur and/or sulfate, thiosulfate, etc.

They use either an organic or inorganic oxidizing agent.

Those based on organic oxidants use sulfonic acid salts of either anthraquinone or naphthaquinone, and other processes with inorganic oxidants use ions of iron, cobalt, and vanadium.

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The processes based on organic oxidants are less desirable because of the low solubility or organic agents in water.

Those using metal ions have a tendency to precipitate metal ions as hydrated oxides and/or sulfides, which result in loss of expensive catalyst as a waste product.

Wastes containing heavy metal ions and sulfides also meet the definition of hazardous waste.

The one-step process, unlike other direct conversion and batch processes, produces an aqueous slurry of sulfur and sodium salt, and is operated at ambient temperatures.

**Spent slurry analysis.** Assessment of a typical spent slurry indicates that the waste is not hazardous, is low in toxicity, and is expected to be practically nontoxic by ingestion with a calculated Oral $LD_{50}$ exceeding 5,000 mg/kg.[13]

The spent slurry was found to have a 96 hr $LC_{50}$ exceeding 500 mg/l. when tested with freshwater fish (fathead minnows).

This is considered to be only moderately toxic according to industry standards.[14]

The chemical analysis (Table 4) shows that the spent slurry contains no hazardous wastes as listed in the federal hazardous waste regulations.[15] The U.S. Environmental Protection Agency (EPA), 14 state agencies, and the U.K. Department of Energy have verified that the typical spent slurry from this one-step process meets the definition of a nonhazardous waste.

**Spent slurry disposal.** Potential disposal methods may include disposal in on site pits, in Class II saltwater disposal wells, at approved commercial disposal sites, and/or offshore.

Each facility operator must evaluate the spent slurry disposal alternatives available based on location, type of facility generating waste, available disposal facilities, and waste stream characterization.

The operator must obtain the necessary disposal permits and/or approvals required at a particular location for a specific facility.[17]

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# Resid hydrocracker expands crude processing flexibility

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Crude oil processing flexibility was expanded with the installation of resid hydroprocessing facilities at Amoco Oil Co.'s Texas City, Tex., refinery. The facilities are used to demetallize and desulfurize resids from heavy, high-sulfur crudes, using a 60,000 b/sd LC-Fining resid hydrocracker.

Conversion in the facilities is adequate to permit the use of existing coker capacity to produce higher-value coke.

**Background.** During the late 1970s and early 1980s, Amoco engaged in an aggressive program committed to processing the heavier, high-sulfur crudes of the future, thus becoming competitive on crude costs. The program mainly involved the Whiting, Ind., and Texas City, Tex., refineries.

The Texas City program, the largest, included two stages. The first stage, named Crude Replacement Program I (CRP I) was completed in 1976 when half of the Texas City crude capacity was converted from low-sulfur crudes to higher-sulfur, medium-gravity crudes. A third delayed coker was required.

The second stage, CRP II, converted the refinery's medium-sulfur crude capacity to process heavier, high-sulfur crudes, and make a higher-value product slate. The pivotal unit was the 60,000 b/sd LC-Fining resid hydrocracking unit.

The total project included a 55,000 b/sd fluid catalytic cracker feed hydrotreater, conversion of two mothballed ammonia plants to hydrogen plants, two 500 ton/day sulfur plants, and a major revamp of a 200,000 b/sd pipestill.

In the initial screening, a number of processing schemes for handling the high-sulfur resid were evaluated. These included delayed coking, Flexicoking, resid fluid catalytic cracking, and consideration of three different boiling range resid feedstocks for hydroprocessing.

The hydroprocessing step accomplished demetallization, desulfurization, and hydrocracking. Unconverted resid was alternatively examined as fuel oil, or feed to delayed coking or resid catalytic cracking.

Overall economics, learning curve opportunities, technical soundness, and flexibility of the process to meet changing requirements were all considered in the process choice. Flexibility was considered particularly important in view of the uncertainties of crude supply, product demands, and governmental controls.

Following the initial studies, the three most attractive options for CRP II were evaluated in detail. They were:

1. A new coker, supplementing existing units, to process the higher yield of vacuum tower bottoms resulting from running 200,000 b/sd of high-sulfur crudes
2. Hydroprocessing facilities to demetallize and desulfurize the resid—with conversion adequate to permit use of existing coker capacity
3. Hydroprocessing and catalytic cracking options required developing new technology to meet Amoco's specific goals.

Fig. 1

Crude-processing section before CRP II

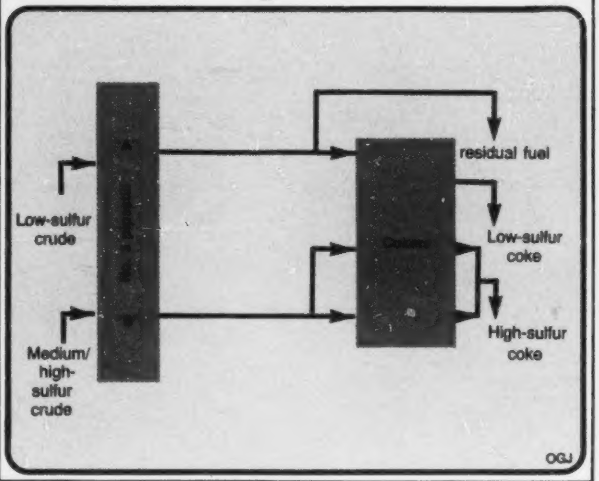
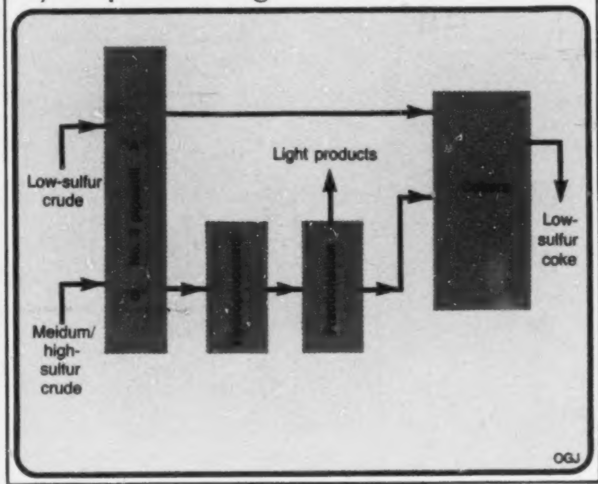


Fig. 2

Hydroprocessing added to crude sec.



A comprehensive study plan was developed in 1977 with a special task force assigned the responsibility of evaluating existing resid hydroprocessing and catalytic cracking processes, and guiding the research and development work.

After intensive process and catalyst development studies and economic evaluations, the resid hydroprocessing case (Case 2), using the existing cokers to produce anode-grade coke, was selected in February 1980. Economic incentives were based on improved yields, lower crude costs, and production of high-value coke.

**Fixed vs. expanded bed.** The choice of the reactor design for the resid hydroprocessor was viewed as critical. Task force members from engineering, the refinery, and research and development inspected fixed-bed resid desulfurization units in Japan, and expanded-bed units in Kuwait and Mexico. Amoco was already a participant in the H-Coal pilot project which used an expanded bed reactor system.

The conclusions of the task force were that while there were many fixed-bed units operating reliably on atmospheric resids, the history of commercial fixed-bed units on vacuum resids was not sufficient to confirm good operability, especially with poor quality crudes. Major concern for the fixed beds was the excessive number of catalyst changeouts required and the tight schedule involved in turning around multiple reactor trains when processing Amoco's design feedstocks. In contrast, the expanded-bed units had demonstrated reliable operations with vacuum resid.

Expanded-bed reactors have a number of advantages. Expanded-bed systems are much more flexible than fixed-bed systems, particularly from the standpoint of being more tolerant of solids formations which normally occur as conversion is increased.

Amoco felt this was critical in positioning itself with the necessary flexibility to process vacuum resids from the uncertain and poor quality feed supplies of the future. The ability to add and withdraw catalyst on stream in the expanded-bed reaction system provided the unique capability to control catalyst activity to meet the demands of the deteriorating quality of future feedstocks.

Other advantages of the expanded bed units include:

- Lower pressure drop and elimination of bed plugging or channeling
- Permissible operations at higher resid conversion as limited by solids and operability
- Lower investments for the same feed and product specifications
- More flexibility to capitalize on anticipated catalyst improvements.

The decision was made to license LC-Fining. Three years after the selection of the LC-Fining process for the Texas City unit, Amoco became a joint licensor of the LC-Fining technology along with Lummus Crest and Cities Service Research & Development.

Amoco brought to this arrangement extensive refinery experience, a strong technology background, a similar philosophy of operations, extensive pilot plant research to support the Texas City unit, and the commercial operation of the unit at Texas City.

The LC-Fining unit was mechanically completed on Nov. 5, 1984, about 3 weeks later than planned, on a schedule that was established almost 3½ years earlier. After initiating the 40-day start-up sequence, resid was charged to the first of the three parallel trains on Dec. 21, 1984, 3 days later than planned. While some problems were encountered, the start-up of the train went very well. Lack of previous hands-on experience with expanded-bed reactors, and variability of gas flows and pressure during initial instrument tuning, resulted in some catalyst carryovers.

Reactor entry was not required because of special catalyst withdrawal lines to clear the pump. Outages were minimized. The hardware performance has far exceeded expectations.

**System description.** A simplified flow diagram of the crude section of the Texas City refinery is shown in Fig. 1. There are two crude units run from the same control room and located on the same site.

The "A" side is designed to process low-sulfur, medium-to-light gravity crudes. The "B" side, originally designed the same way, was converted to process the higher-sulfur, medium-gravity crudes in 1976—our so-called Crude Replacement Program I.

Before CRP II, the bottoms from these pipestills were charged to three cokers capable of processing about 40,000 b/sd of resid and producing 2,000 tons/day of coke. Some of the low-sulfur resid can be split between fluid catalytic cracking and low-sulfur fuel oil production. Gas oils are processed in three catalytic cracking units, with a total capacity of about 175,000 b/sd.

A simplified flow diagram of the refinery after the completion of CRP II is shown in Fig. 2. The heavier, high-sulfur crude blend is run on the "B"

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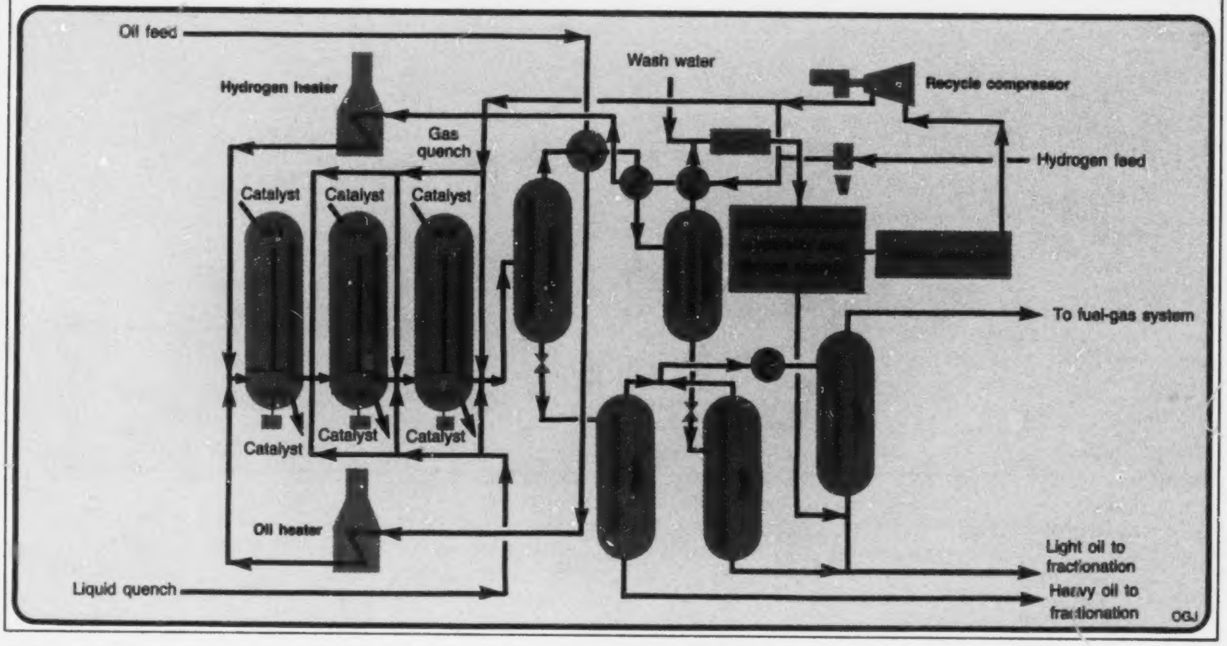
Based on a paper presented at the National Petroleum Refiners Association annual meeting, Los Angeles, Mar. 23-25.

Fig. 3

Flow diagram of one-reactor train



side of the crude unit. Low-sulfur crude continues to be run on the "A" side.

The high-sulfur vacuum resid from the "B" side is processed in the new 60,000 b/sd LC-Finer. Low-sulfur resid from the "A" side is generally split between catalytic cracking and delayed coking, but some low-sulfur resid has been charged to the LC-Finer. In the LC-Finer, the resid is converted to catalytic cracker feed and lighter products, and the unconverted desulfurized resid is sent to the delayed coking units.

Heavy coker gas oil and high-sulfur, heavy vacuum gas oil are charged to a 55,000 b/sd cat feed hydrotreater which started up in November 1983, as the first phase of our CRP II project.

The basic advantages of the resid hydroprocessing/coking combination over coking alone are:

- The LC-Fining/coking combination makes a higher volume of more valuable liquid products and less coke. These liquid products are lower in sulfur and nitrogen. Because of hydrogen uptake in the hydroprocessor, they have a higher hydrogen-to-carbon ratio and are superior feedstocks for downstream processing.
- The sulfur and metal levels in the remaining unconverted resid enable production of higher-value anode coke. The base design case for the LC-Fining unit was 60,000 b/sd of resid, 60% conversion to lighter liquid products, 62% reduction in carbon (Ramsbottom measurement), 80% desulfurization, and 88% demetallization.

As with most new units, there have been major differences between the design feed compositions and the actual feedstock compositions processed by the unit. The range of feedstock qualities charged to the LC-Finer in 1985 are shown along with design qualities in Table 1.

The differences between the design feed and the actual feeds are related to the availability of crudes to the Amoco refining system. In the initial conception of CRP II, Amoco had anticipated processing its proprietary Ardeshir (Aboozar) crude from Iran.

The design blend shown in the table was chosen as being a crude composition which we wanted to be able to process if it was available. Diluent is blended into vacuum resid to improve the overall operation of the unit.

During the year, resid feed metals ranged from 180 to 550 ppm. In the last quarter of 1985, the unit has charged more difficult resids with an average metals content of 450 ppm. The feed blend comes from a wide range of crude sources. All were processed satisfactorily, even though pilot plant work showed some of these resids produced high solids concentrations with potential commercial operating problems.

**LC-Fining details.** The LC-Fining unit as constructed at Texas City consists of the following sections:

1. Makeup gas compression
2. Demetallization and desulfurization reactors
3. Low-pressure gas recovery and purification
4. Fractionation using atmospheric and vacuum towers
5. Catalyst handling

The reactor section has three independent parallel trains with three reactors per train. The unit is designed to operate with one, two, or all three trains in service. Each train is provided with one demetallization and two desulfurization reactors. The other sections serve all three reactor trains.

A simplified flow diagram of one of the reactor trains is shown in Fig. 3. Equipment in the reactor train includes feed preheat exchangers, oil and hydrogen furnaces, the three reactors, reactor effluent separation, and recycle gas purification.

Oil is preheated against reactor effluent in a feed/effluent exchanger. Feed normally consists of vacuum resid with a heavy vacuum gas oil diluent. The feed is further heated in an oil heater.

The exothermic reactions increase the reactor temperature to the desired operating level. The first reactor, R-1, is a demetallization reactor designed to remove metals from the vacuum resid feed. Metals removal was essential to protect the desulfurization catalyst and for anode-grade coke production.

Reactors R-2 and R-3 are desulfurization and Rams carbon conversion reactors, removing a substantial amount of sulfur from all reactor products. Hydrocracking occurs in all three reactors.[1]

A schematic of an LC-Fining reactor is shown in Fig. 4. Feed oil and gas

Fig. 4

## LC-Fining reactor

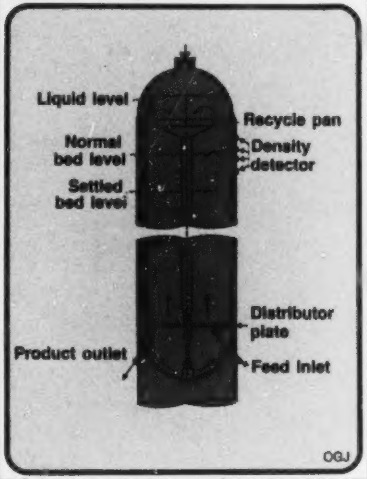


Table 1

## LC-Finer feedstock data

| | Vacuum resid | |
|---|---|---|
| | Design | Commercial unit |
| Gravity, °API | 2.8 | 4.6-7.8 |
| Sulfur, wt % | 5.5 | 2.7-3.9 |
| Rams carbon, wt% | 21.5 | 16.4-20.4 |
| Metals, ppm | 340 | 180-550 |
| 1,000° F, vol % | 3 | ~8 |

| | Vacuum resid with diluent | |
|---|---|---|
| | Design | Commercial unit |
| Gravity, °API | 5.8 | — |
| Sulfur, wt % | 5.1 | — |
| Rams carbon, wt% | 17.4 | — |
| Metals, ppm | 274 | — |
| 1,000°D, vol % | 28 | — |
| Diluent, vol % | 20 | 20 |

Table 2

## Typical product qualities*

| | Gravity, API | Sulfur, wt % | Nitrogen, ppm | Rams carbon, wt % | End pt., °F. |
|---|---|---|---|---|---|
| Heavy naphtha | 48 | 0.01 | 300 | — | — |
| Light distillate | 38 | 0.04 | 600 | — | 550 |
| Middle distillate | 32 | 0.25 | 1100 | — | 675 |
| LGO/Vac. naphtha | 28 | 0.30 | 2000 | — | — |
| Light VGO | 23.5 | 0.30 | 2500 | 0.2 | — |
| Heavy VGO | 20.0 | 0.45 | 3500 | 0.4 | — |
| Vac. resid | 9.5 | 1.20 | — | 16.0 | — |

*Resid hydrotreating unit

enter at the bottom of the reactor and join a moving recycle oil stream. The mixture passes up through a distributor plate at sufficient velocity to expand the catalyst above the grid into a state of random turbulent motion.

The expanded bed is maintained at about 35% above the settled level by closely controlling the recyle oil pump speed and monitoring the density detectors. Suction to the recycle pump is supplied from near the top of the reactor. A recycle pan is provided to disengage the gas before recycling the liquid.

Temperature control in the reactors is accomplished by carefully monitoring temperatures at several levels and radially around the reactors. The hydrogen heater is fired to control the temperature of the first reactor.

Naphtha and hydrogen quenches to the inlets control the second and third reactor temperatures. Pressure control of the recycle gas compressor suction is accomplished by makeup hydrogen gas addition.

Reactor effluent separation takes place in a series of separators and flash drums at high, medium, and low temperature levels. Reactor effluent from the third reactor goes directly to the high-temperature separator where the initial separation of vapor and liquid takes place. The vapor from the high-temperature separator is cooled against feed and recycle gas in heat exchangers.

After separation from liquid in the medium-temperature separator, the hydrogen vapor is further cooled with an air cooler. Process wash water is added to remove ammonium poly sulfides.

The water and hydrocarbon liquid are separated from the vapor in the low-temperature separator. The remaining vapor is contacted with sponge oil to remove other light ends and thus improve recycle gas hydrogen purity.

The recycle gas is further contacted with monoethanolamine (MEA) to remove hydrogen sulfide. The liquid from the high, medium, and low temperature separators is let down in pressure in flash drums. The vapor is further processed to recover propane and heavier components in the hydrogen. The liquid feeds the fractionation section.

The makeup hydrogen gas compressor system consists of six, 8,000 hp, reciprocating compressors. Three or four are normally utilized depending upon operating conditions. The other machines are spares and permit on-stream maintenance.

The high electric load of these and other compressors and motor drives in the resid and cat feed units required a 100,000 kw electric system expansion at the refinery. A 180,000 kw cogeneration plant, producing 1.2 million lb/hr of steam is under construction to economically serve this expanded load. It will be operational by mid 1986.

A simplified diagram of the fractionation system is shown in Fig. 5. Fractionation is the same as in a conventional crude unit, consisting of an atmospheric tower and a vacuum tower with associated charge heaters.

The products are naphtha, light distillate, middle distillate, light gas oil, light and heavy vacuum gas oils, and desulfurized vacuum resid. There is also a vapor recovery unit to fractionate the naphtha products and to recover light ends. Typical product qualities are shown in Table 2.

**Catalyst handling.** A simplified diagram of the catalyst-handling system is shown in Fig. 6. This system consists of three sections; fresh-catalyst handling, daily addition/withdrawal of catalyst to and from the reactors, and spent-catalyst handling.

Fresh demetallization catalyst is slurried, with heavy vacuum gas oil, from the high pressure transfer vessel to the first reactor in each train. Fresh desulfurization catalyst is slurried to the third reactor in each train. Desulfurization equilibrium catalyst is withdrawn from the third reactor and slurried to the second reactor in each train.

Spent catalyst is withdrawn from the first and second reactors and sent to the transfer vessels. It is washed, cooled, slurried, and sent to spent catalyst handling inventory vessels.

The Texas City unit has the capability of handling two different catalysts. Because of this design, the system is not configured to cascade catalyst from the second to the first reactor.

**Plant arrangement.** An aerial view of the CRP II facilities is shown in Fig.

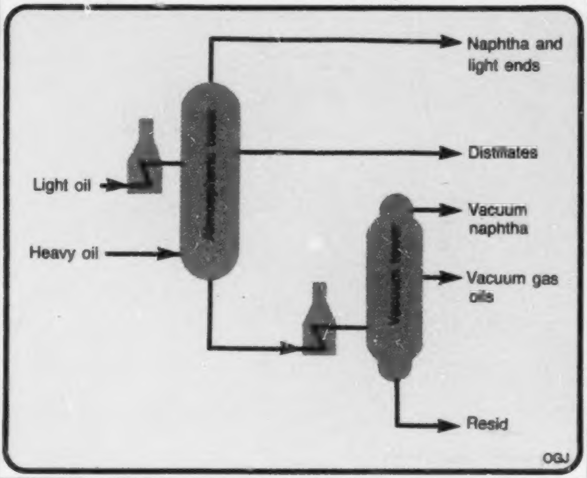


Fig. 5

Fractionation section diagram

Naphtha and light ends
Distillates
Light oil
Heavy oil
Vacuum naphtha
Vacuum gas oils
Resid
OGJ

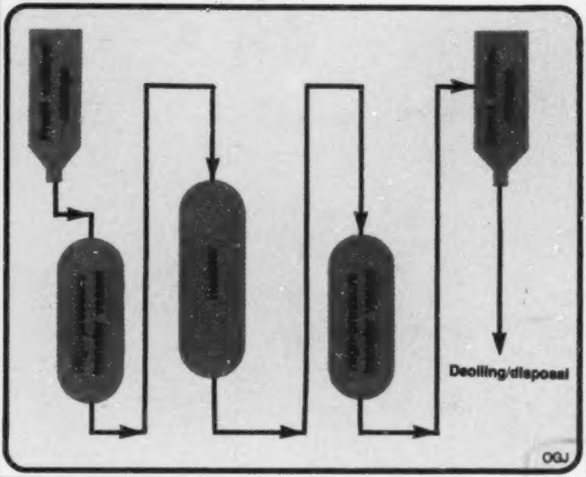


Fig. 6

Catalyst handling system

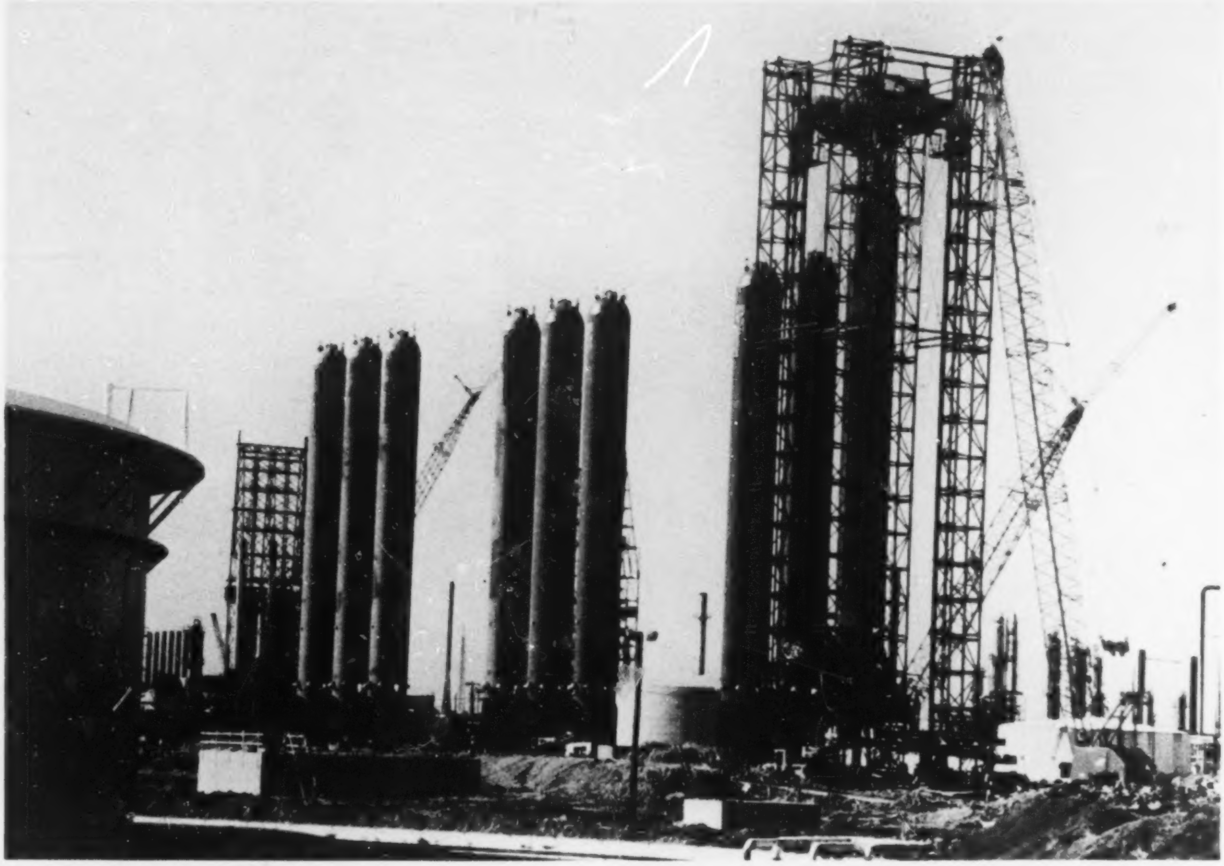
Deoiling/disposal
OGJ

7. The nine resid hydrocracker reactors are visible on the lower left side of the plant. The atmospheric and vacuum towers are on the far left side of the plant.

The catalyst monorail system is shown on the right side of the plant, just above the storage tank. It runs from the staging building at the far right to the storage silos at the right side of the plant.

After site clearance, the reactors,

**Hydrocracking reactors,** heaters, fractionation section, and catalyst handling monorail (lower right) are visible in this aerial view of Amoco's heavy-oil-processing facility (Fig. 7).



**The nine hydrocracking reactors** shown during construction of the plant (Fig. 8).

built in Japan and shipped on a specially built, ocean-going vessel, arrived precisely on time. The reactors were transferred from the docks to the refinery on a multiwheeled transporter, pulled by a 1,000-hp mining truck.

The transporter has 384 wheels, each hydraulically loaded, and combined into 12-wheel, steerable trucks. Because of the length of the vessel, and the curves that had to be negotiated, the vessel rested on two turntables mounted on the transporter.

The reactors are the largest shop fabricated vessels in the world. They are 100 ft from tangent to tangent, 14-ft diameter, have 12-in. thick walls, and weigh 1,150 tons each, without internals.

It took 45 days to lift the nine reactors into place. Each lift required about 9 hr and 3 to 4 days to move the jacking system to the next foundation without dismantling.

The reactors were lifted by a four-mast hydraulic jacking mechanism. This was truly an international event. The reactors were built in Japan, shipped on a Japanese-built ship of Panamanian registry, moved to the refinery by an American rigging company using a German transport system. The lift system was built in Sweden, is owned by a British company and operated by a British crew.

Fig. 8 shows the nine LC-Fining reactors, taken as the last reactor was being lowered to its foundaton.

The LC-Fining complex is a medium-size refinery in itself. A photo of the vacuum tower and atmospheric tower is shown in Fig. 9. This section is essentially built like a 75,000 b/sd crude unit. There is also a small vapor recovery section.

**Unit performance.** the first reactor train (300) came on stream with resid on Dec. 21, 1984—right on schedule. Resid was injected into the second train (400) on Jan. 8, 1985. The third train (200) was on stream and continuously injected with resid on Mar. 28, 1985. The average throughputs and average conversions for the first year of operation were 47,400 b/cd and 62,700 b/sd; and 59% conversion of the 1,000° F.+ material and about 60% of the Rams carbon. There were several periods of operation at above 75% conversion of the 1,000° F.+ material.

Sulfur removal ranged from 80 to 90% and metals removal was 85 to 95+%. Typically, we operate the unit at maximum Rams carbon removal. However, if excessive solids concentrations are observed, corrective actions are taken.

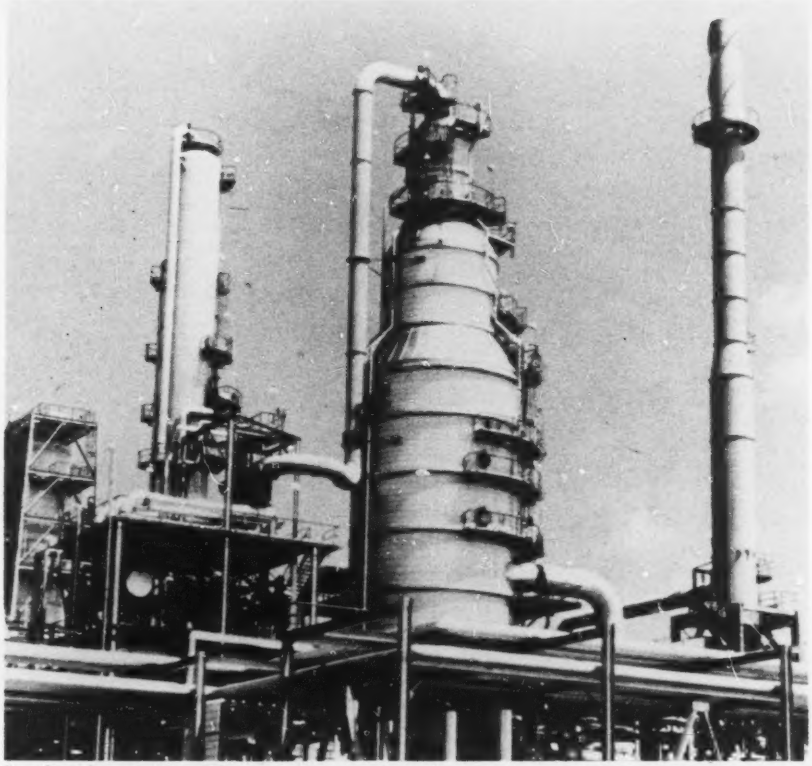
These involve raising catalyst addition rates and lowering resid concentrations. During our learning process with some of the worlds most difficult resids, solids problems have occurred. Solids are noted in the fractionation section, particularly by plugging of the bottoms pump screens.

The operating factors for the three trains during the first year are summarized in Table 5. The average operating factor for the three trains is 80.8%.

These operating factors are based on days of operation when resid is charged to the unit. The main causes of resid outages are recycle pump electrical failures, recycle gas compressor seal failures, and catalyst carryover.

Problems with the recycle pump electrical equipment have been corrected. In most cases, catalyst carryover only results in brief resid outages because we are able to clear the pump suction line using the pump itself, and the special catalyst withdrawal lines. Vacuum gas oil charge is continued during the pump suction line clearing procedure.

**Catalyst addition/withdrawal.** Amoco's catalyst is brought in by rail-



**Fractionation section** of the LC-Fining complex is built like a 75,000-b/sd crude unit (Fig. 9).

road from three catalyst manufacturers located in the midwestern and eastern United States. The catalyst is trucked from the rail yard in Houston to the Texas City refinery.

The catalyst, in 5-ton containers, is carried from the staging area to the fresh catalyst silos by a monorail system. From the silos it is pneumatically conveyed in dense phase to the day hoppers.

Heavy vacuum gas oil is used to transport the catalyst in slurry form to the reactors after it is received from the day hoppers and the catalyst transfer vessels. Likewise, spent catalyst is removed from the reactors with a vacuum gas oil slurry and received in high-pressure catalyst transfer vessels.

The control of the daily addition/withdrawal catalyst handling system is executed by a Foxboro 1/A computer. It involves 110 to 150 sequential steps—opening and closing of valves and starting and stopping of process flows. The Foxboro 1/A computer is interlocked with programmable logic computers which prevent valves from opening until process pressure, temperature, and other valve positions are correct. Typically, about 12,000 lb of catalyst are added per cycle. The design cycle time for the demetallation system is about 9 hr, and the cycle time for the desulfurization system is about 11 hr. However, the actual average times are about 14 hr and 16 hr, respectively.

Catalyst additions, of course, are not on a continuous basis. The number of additions depends upon the optimum catalyst usage.

Catalyst addition was not required until the catalyst had aged. Catalyst addition was begun on the 300 and 400 trains on Apr. 1, 1985, and routine replacement in the 200 train was started on May 27, 1985.

The optimum rate is selected by optimizing between catalyst activity and reactor performance. Based on feedstock quality, the optimum addition rate was determined to be 75% of the design rate. Actual catalyst additions, after beginning continuous catalyst addition in all three trains, were very close to the optimum rate.

**Further work.** Amoco and Lummus Crest have a strong research program aimed at improving the commercial operations of the system. Emphasis is on increasing resid conversion. In addition, because Amoco is using the combination of resid hydroprocessing plus delaying coking, we will continue to emphasize improvements in hydroprocessing and coking which lead to increased quantity and quality of liquids from the combined processes, while maximizing value of the coke produced. Catalyst development includes work in increasing metals tolerance, resid hydrogenation activity, and Rams carbon-removal activity. ▪

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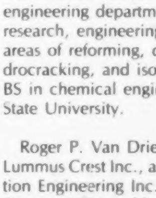
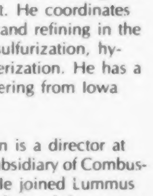


**Petersen**



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# New fixed-bed absorbent for gas sweetening

**P.J.H. Carnell**
Billingham
England

A new granular zinc oxide absorbent for gas or liquid desulfurization has been in service for over 18 months, and over 10 charges have now been used on gas desulfurization. Widespread usage is expected for gas and liquid desulfurization.

## Gas sweetening

Since the early sixties, the main hydrocarbon feedstocks used by the chemical industry have been low-molecular-weight hydrocarbons. These range from natural gas to naphtha, with natural gas and associated gases being those most widely used.

Hydrogen is obtained from these feedstocks by endothermic reforming reaction with steam over a nickel catalyst. The reaction is carried out at high temperatures (about 1,500° F.) in large furnaces containing several hundred alloy-steel tubes packed with catalyst.

The nickel catalyst has high activity and high selectivity and under ideal conditions can last for many years. However, nickel catalysts are easily poisoned by sulfur. The sulfur reacts to form nickel sulfide which does not catalyse the steam-reforming reaction; therefore, hydrocarbon cracking occurs with the formation of carbon and unsaturated hydrocarbons.

The carbon deposits on the catalyst and eventually blocks the tubes. This causes overheating and may result in the tube rupturing. Even small levels of sulfur can have a harmful effect. Industry has had to develop systems for the almost total removal of sulfur (down to less than 0.1 ppm) from feedstocks.

Because nearly complete removal is required, physical absorption processes cannot be used. These would only remove a portion of the sulfur compounds present. Instead, a chemical reaction is used because the level of sulfur remaining is ultimately controlled by the stability of the sulfur compound formed and not by the partial pressure of hydrogen sulfide present in the feedstock.

The desulfurization process is carried out in two stages. In the first, all of the sulfur compounds present are converted to hydrogen sulfide by hydrogenolysis over a cobalt molybdate catalyst.

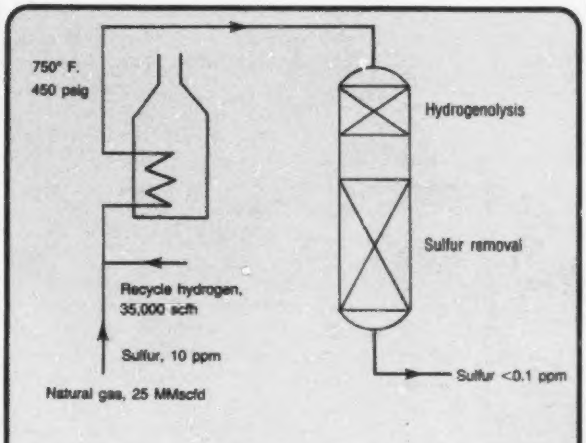
$$RSH + H_2 = RH + H_2S$$

In the second stage, the hydrogen

Based on paper presented at 36th Laurence Reid Gas Conditioning Conference, Norman, Okla., Mar. 3-5, 1986.

Fig. 1

Typical feedstock desulfurization*

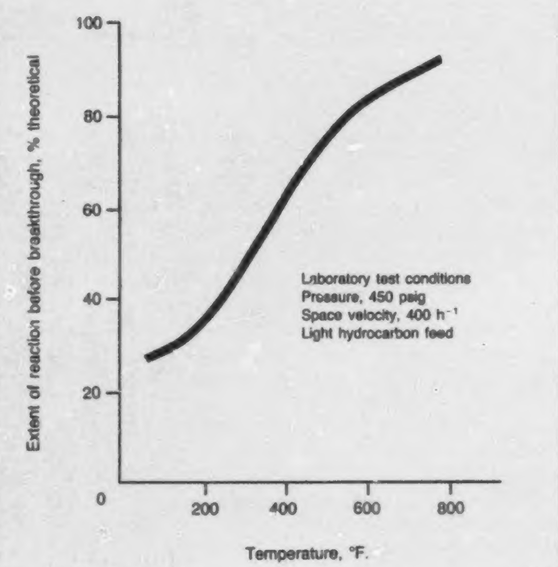


| Catalyst duty | Catalyst type | Vol, cu ft | Dia., ft | Ht., ft | ΔP, psi | Catalyst life, yr |
|---|---|---|---|---|---|---|
| Hydrogenolysis | CoMo | 350 | 7.5 | 7.5 | 1.0 | 7 |
| Sulfur removal | ZnO | 1,000 | 7.5 | 22.5 | 1.5 | 2† |

*for a 1,000 ton/day ammonia plant †Catalyst changes at plant shutdown OGJ

Fig. 2

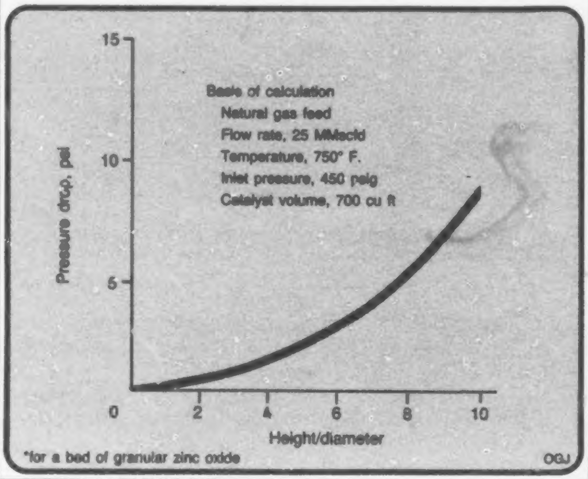
Absorption of sulfur by zinc oxide*



*as a function of temperature OGJ

Fig. 3

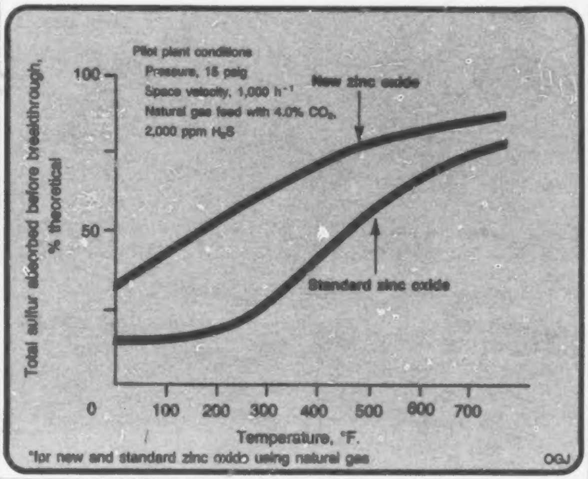
## Pressure vs. height-to-diameter ratio*



*for a bed of granular zinc oxide

Fig. 4

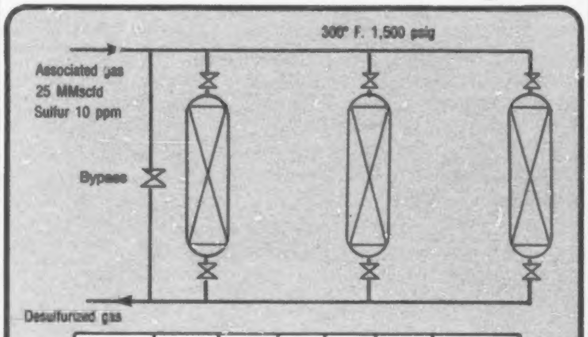
## Accelerated breakthrough tests*



*for new and standard zinc oxide using natural gas

Fig. 5

## Desulfurization for associated gas*

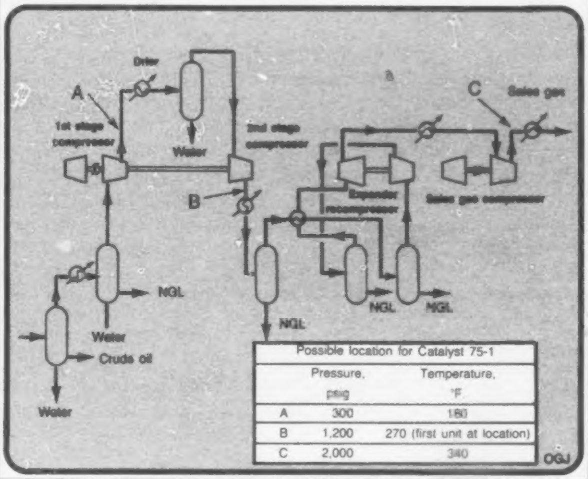

300° F. 1,500 psig
Associated gas
25 MMscfd
Sulfur 10 ppm
Bypass
Desulfurized gas
OGJ

| Catalyst duty | Catalyst type | Vol, cu ft | Dia., ft | Ht., ft | ΔP, psi | Catalyst life, yr |
|---|---|---|---|---|---|---|
| Sulfur removal | ICI 75-1 | 3 × 130 | 3.25 | 15 | 10 | 0.5 + † |

*on an offshore platform †Beds changed one at a time at convenient intervals when sulfur slip unacceptable

Fig. 6

## Flowsheet for offshore oil platform


Drier
A
1st stage compressor
Water
2nd stage compressor
B
Expander recompressor
C
Sales gas
Sales gas compressor
NGL
Water
Crude oil
Water
NGL
NGL
NGL
OGJ

| Possible location for Catalyst 75-1 | | |
|---|---|---|
| | Pressure, psig | Temperature, °F |
| A | 300 | 180 |
| B | 1,200 | 270 (first unit at location) |
| C | 2,000 | 340 |

sulfide is removed by the reaction with granular zinc oxide packed in fixed beds.

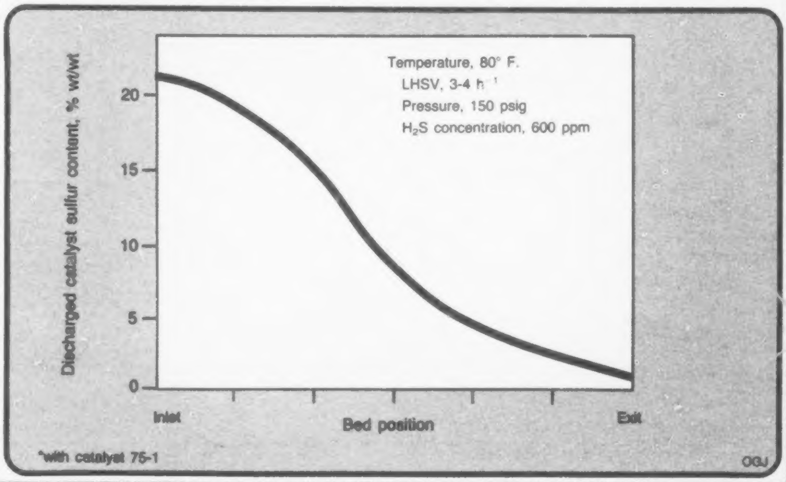
$$ZnO + H_2S = ZnS + H_2O$$

Desulfurization is carried out during the gas preheat stage before the reformer. Normal process conditions are 750° F. and 450 psig. A typical 1,000-ton/day ammonia plant would use about 25 MMscfd of natural gas containing up to 50 ppm of sulfur (expressed as hydrogen sulfide). This would be processed using a single reactor containing 350 cu ft of cobalt molybdate catalyst and 1,000 cu ft of zinc oxide. Fig. 1 shows a typical flow sheet for desulfurization.

This process is used widely in the chemical industry. There are now over 400 large plants operating throughout the world using large beds

Fig. 7

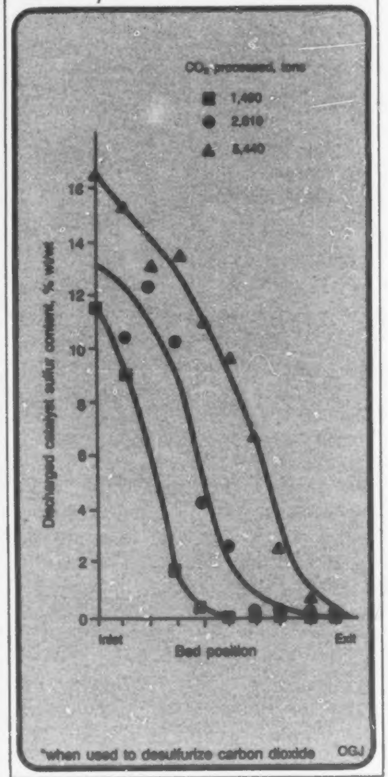
## Desulfurization of liquid butane*



*with catalyst 75-1

Fig. 8

## Catalyst 75-1*



*when used to desulfurize carbon dioxide

OGJ

Table 1

## Typical composition of associated gas from a North Sea oil production platform

| Component | %, vol/vol |
|---|---|
| Methane | 60.0 |
| Ethane | 14.0 |
| Propane | 15.0 |
| Butanes | 5.0 |
| Pentanes | 1.5 |
| Hexanes | 0.2 |
| Heptanes | (0.03) |
| Nitrogen | 0.7 |
| Carbon dioxide | 3.6 |
| Hydrogen sulfide | 10 ppm |

Table 2

## Design and operating conditions for desulfurization of North Sea associated gas

| | Design | Operating |
|---|---|---|
| Temperature, °F. | 300 | 275-340 |
| Pressure inlet, psig | 1,250 | 1,130-1,235 |
| Space velocity, $h^{-1}$ | 3,000 | 4,100-7,400 |
| $H_2S$ inlet, ppm | 10 | 1.0-8.0 |

of granular zinc oxide as the final stage in gas desulfurization. There are several hundred small beds of zinc oxide in small plants or on general guard-bed duty for related processes.

**Reaction of ZnO with $H_2S$.** Zinc oxide is used as the chemical absorbent because of the great stability of zinc sulfide. Under all operating conditions (ambient to 750° F.), zinc sulfide is the most stable species. Also, neither zinc oxide nor zinc sulfide reacts with steam, hydrogen, water, or hydrocarbons.

The absorption process is a gas/solid reaction and, therefore, the rate of reaction is controlled by diffusion processes. Each molecule of hydrogen sulfide must first diffuse to the surface of the zinc oxide and then react to produce a sulfide ion and water.

The water must diffuse out, and the sulfide ion must diffuse into the interior of the crystal and replace the oxide ions until the whole structure is changed from zinc oxide to zinc sulfide. The sulfide ion is much larger than the oxide ion and, as there is no increase in overall size of the particles, this change causes loss in porosity and severe structural distortion. The rate of lattice diffusion is slow at low temperatures, and zinc oxide is conventionally only considered as a hot desulfurization catalyst. The extreme sensitivity to temperature of conventional zinc oxide is shown in Fig. 2.

The strong dependence on lattice diffusion means that other process factors such as space velocity and pressure have relatively little effect on the operating efficiency of zinc oxide.

Hydrogen sulfide is removed by chemical reaction to form zinc sulfide. An absorption profile is formed which passes down the bed, and the zinc oxide is considered spent when hydrogen sulfide slip is observed. The shape of the absorption profile is governed by the process conditions and the formulation of the zinc oxide catalyst used.

The shape of the absorption profile is reproducible and it is possible to predict its rate of progress for given process conditions.

Many operators use beds in series so that one can be fully saturated before it is changed. Tall thin beds lessen the risk of channeling and make part-bed change outs easy. The absorbent beds offer little resistance to flow, and the pressure drop of deep beds is surprisingly low. The relationship between pressure drop and height-to-diameter ratio for a given volume of absorbent and constant gas rate is shown in Fig. 3.

All of these data were produced using commercially available oxide.

**New zinc oxide catalyst.** Having identified the importance of the diffusion processes in controlling the reactivity of zinc oxide, we examined ways of altering the structure to increase the activity of the zinc oxide. We found that by making a slight reduction in density we could greatly increase porosity and surface area without significantly altering the crushing strength or the attrition loss.

The new absorbent shows greatly improved low-temperature activity. This is illustrated in Fig. 4, which compares the performance of conventional high-temperature zinc oxide with the new product. The higher activity of the new product clearly opened a number of possibilities for the low-temperature desulfurization of hydrocarbons under conditions not previously considered economically viable.

**Desulfurization of associated gas.** The first commercial use for the new material was the desulfurization of associated gas on a North Sea oil platform.

In general, oil from the North Sea contains little sulfur, and the associated gas is almost sulfur-free. The gas is taken ashore by undersea pipelines for delivery to the U.K. natural-gas grid. Because of the very low sulfur content of the oil, this distribution system is designed with a pipeline specification for hydrogen sulfide of 3.3 ppm.

No problems were encountered during the early years of operation. Recently, seawater injection has been adopted on a number of platforms and this has introduced sulfate-reducing bacteria (SRB) to the oil fields. These are now generating hydrogen sulfide, and there is concern that the pipeline specification will be exceeded. Therefore, operators are interested in removing hydrogen sulfide from the gas on the platform.

It is obviously difficult to retrofit a desulfurization unit on an offshore platform. There are severe restrictions on space and weight, and there are no convenient sources of heat for a regenerable system. Hence, the use of a fixed-bed absorbent holds a number of attractions.

The new absorbent has high activity at low temperature, but the activity still improves as the temperature is increased. Hence, it was decided to install the catalyst downstream of a compressor to take advantage of compression heat. Space-and-weight constraints meant that it was not possible to use a single reactor. Also it was decided to use the platform crane to

Table 3

## Range of liquids tested for sulfur removal by new absorbent

| Liquid | Temperature, °F. | Pressure, psig | Sulfur type |
|---|---|---|---|
| Propylene | Ambient | 265 | $COS/H_2S$ |
| Hexane | 120 | 0 | $H_2S$ |
| Kerosine | 100 | 0 | $H_2S$ |
| Butane | 80 | 150 | $H_2S$ |

Table 4

## Process conditions for the desulfurization of carbon dioxide by absorbent

| | |
|---|---|
| Temperature, °F. | 60-70 |
| Pressure, psig | 650-700 |
| Space velocity, $h^{-1}$ | 500 |
| $H_2S/COS$, ppm | 25 |
| $CH_3SH$, ppm | 0.3 |
| RSH, ppm | 1.3 |

### The author...

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install the unit, and this set a maximum weight limit on any one item.

The final arrangement chosen was three beds in parallel, each containing 130 cu ft of the new absorbent. This allows the platform to operate 6-8 months at full gas production before a change is needed. The units have been in operation for 18 months and have proved completely reliable. A typical composition of the gas being desulfurized is given in Table 1.

The design and range of operating conditions are given in Table 2, and the vessel layout is given in Fig. 5.

Monitoring the hydrogen-sulfide content at sample points down the beds has confirmed that the absorption profile progresses slowly and predictably through the bed. The spent catalyst is discharged by gravity flow and contains in excess of 20% wt/wt sulfur in a stable nonodorous form. Discharged zinc oxide is normally sold for metals recovery.

The success of these units has been of interest to a number of operators, and similar installations are being designed. Fig. 6 shows a typical flowsheet for an offshore oil-production unit and the three most suitable locations for the process.

It is a feature of the process that one molecule of water is produced for every molecule of hydrogen sulfide removed. Hence, if the level of hydrogen sulfide to be removed is high, the units should be located upstream of the drier. If a small amount of water is produced, the units can be installed downstream of the final gas compressor.

In service, the gas flow is split between the beds of zinc oxide and the bypass to give the required degree of desulfurization.

**Desulfurization of liquid hydrocarbons.** The new absorbent has been tested with associated gas at pressures up to 1,500 psig and temperatures from 25 to 750° F. It functions predictably throughout this range of conditions. Clearly, under some of these conditions, the hydrocarbons are close to condensation, and so tests have been carried out with liquid hydrocarbons.

We have shown that the new absorbent will remove carbonyl sulfide and hydrogen sulfide from a number of liquid hydrocarbons.

The liquids tested to date are given in Table 3.

These data are of interest to a number of oil companies, and several possible applications for the removal of hydrogen sulfide from liquid hydrocarbons are now being considered.

**Desulfurization of carbon dioxide.** Zinc oxide can be used to desulfurize carbon dioxide. Carbon dioxide reacts to a certain extent with zinc oxide, but carbon dioxide is displaced by hydrogen sulfide to form the more stable zinc sulfide.

The new absorbent is being used in Australia to remove hydrogen sulfide and carbonyl sulfide from naturally occurring carbon dioxide prior to use in the soft drink industry. The process conditions being used are given in Table 4.

The absorbent is used in beds arranged in series. Absorption profiles, obtained with three charges used for the processing of different amounts of carbon dioxide, are shown in Fig. 7. These illustrate the highly predictable nature of the absorption profile.

**Advantages of the new absorbent.** The use of a fixed bed of granular zinc-oxide absorbent for gas or liquid desulfurization offers a number of process advantages.

1. It is a very simple process.

There are no pumps, motors, or control loops. Apart from charging and discharging, there are no operating requirements. The units can be left unattended.

2. It has a low capital cost.

The capital cost of a bed of zinc oxide is low when compared to the cost of systems which require recirculation pumps or regeneration units.

3. It can handle wide variations in flow and levels of hydrogen sulfide.

Because it is a simple absorption process with a solid absorbent, very wide variations in flow rate can be accommodated. There is no liquid to foam or carryover. Changes in the amount of sulfur merely affect the changeover frequency.

4. It can be easily retrofitted.

In its simplest form, all that is required is a vessel and two isolation valves. The unit can easily be coupled into an existing process line.

5. It can be used at any pressure.

Pressure has almost no effect on the reaction kinetics. It can be used at any pressure, and pressure cycles will not affect the performance.

6. It can be used at any temperature.

The efficiency of reaction is improved with temperature, but heat is not specifically required. There is no need for heaters or reboilers and any convenient temperature may be used.

7. There are no safety or environmental problems.

The fresh and spent zinc oxide are always in the form of solid granules. Neither product is injurious to health and both are readily salable to a number of outlets.

8. Long operating life.

Zinc oxide has great stability, so beds of it have very long lives. The normal life is 4-8 years. In an extreme case, a charge was recently removed from a U.K. Plant after 17 years in service. The zinc oxide is only consumed when hydrogen sulfide has to be removed.

9. Handling is easy.

The absorbent is in the form of free-flowing granules. These do not cake in service, and straightforward gravity charging and discharging are used at changeouts. Some operators discharge by suction from the top of the vessel.

10. The technology is well established.

The new absorbent is a development of well-established product. This means that only limited extrapolation is needed to produce an accurate prediction of performance. ▪

# Calculation method simulates LPG/$H_2S$ MEA

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It is sometimes difficult to simulate monoethanolamine (MEA) liquid-liquid contactors, especially when chemical reactions occur in addition to physical equilibrium considerations. For example, when $H_2S$ is removed from LPG from a fluid catalytic cracking unit (FCCU), two phenomena occur during the extraction process:

- $H_2S$ is absorbed into the aqueous phase through physical equilibrium which includes concentration gradients and $H_2S$ solubility into the aqueous or organic phase
- $H_2S$ reacts with MEA dissolved into the aqueous phase, according to the equation:

$$H_2S + OH-CH_2-CH_2-NH_2 \rightarrow OH-CH_2-CH_2-NH^+_3-SH^- \qquad (1)$$

An alternate method of calculation can simulate contactors when chemical reactions are present. The method uses an algorithm that calculates a mass balance by a rigorous, tray-by-tray approach, taking into account the effect of the chemical reaction between the components at each stage.

**Method development.** The calculation method is developed by considering a typical theoretical stage as shown in Fig. 1. If a chemical reaction takes place inside stage J, the component mass balance can be represented:

$$h_{j-1-i} + a_{j+1,i} + S_i \times RM_j - h_{j,i} - a_{j,i} = 0 \qquad (2)$$

where:

$h_{j-1,i}$ = Molar flow of component i in the organic phase entering stage J

$a_{j+1,i}$ = Molar flow of component i in the aqueous phase entering stage J

$S_i$ = Stoichiometric coefficient of component i in reaction 1

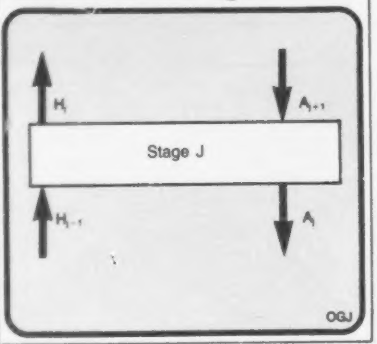
$RM_j$ = Reacted moles of $H_2S$ per unit time at stage J

$a_{j,i}$ = Molar flow of component i in the aqueous phase leaving stage J

$h_{j,i}$ = Molar flow of component i in the organic phase leaving stage J

Fig. 1

Theoretical stage



In order to maintain the validity of Equation 2, if component i is a reaction product, its stoichiometric coefficient must be positive. If the component is not a reaction product, the stoichiometric coefficient must be considered as negative.

It is also assumed that the chemical reaction between $H_2S$ and MEA takes place in the aqueous phase and is rate controlled. Using the Kent-Eisenberg model[1] and maintaining the stoichiometric coefficient requirements to keep Equation 2 valid, the equilibrium reaction equation can be expressed:

$$K_j = X_{j,HS-} \times A_j^z \times (X_{j,MEA} \times X_{j,H_2S})^{-1}/DML \qquad (3)$$

where:

$K_j$ = Equilibrium reaction constant under conditions of stage J

$X_{j,HS-}$ = Molar fraction of MEA sulfide in aqueous phase on stage j

$A_j$ = The aqueous phase molar flow leaving stage J

z = Algebraic sum of the stoichiometric coefficients

$X_{j,MEA}$ = Molar fraction of MEA in the aqueous phase on stage J

$X_{j,H_2S}$ = Molar fraction of $H_2S$ in the aqueous phase on stage J

DML = Aqueous phase molar density

Table 1

### Matrix of values obtained from Equation 9

$$\begin{bmatrix} \frac{\partial B_1}{\partial RM_1} & \frac{\partial B_1}{\partial RM_2} & \cdots & \frac{\partial B_1}{\partial RM_n} \\ \frac{\partial B_2}{\partial RM_1} & \frac{\partial B_2}{\partial RM_2} & \cdots & \frac{\partial B_2}{\partial RM_n} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \frac{\partial B_n}{\partial RM_1} & \frac{\partial B_n}{\partial RM_2} & \cdots & \frac{\partial B_n}{\partial RM_n} \end{bmatrix} \begin{bmatrix} \Delta RM_1 \\ \Delta RM_2 \\ \cdot \\ \cdot \\ \cdot \\ \Delta RM_n \end{bmatrix} \begin{bmatrix} B_1 \\ B_2 \\ \cdot \\ \cdot \\ \cdot \\ B_n \end{bmatrix}$$

The reflux ratio is defined as the ratio of the aqueous phase flow to the organic phase flow in any stage, and the extraction factor is defined as the ratio of reflux ratio to equilibrium constant. They are expressed as:

$$R_j = A_j/H_j \qquad (4)$$

$$E_{j,i} = A_j/(H_j \times k_{j,i}) \qquad (5)$$

where:

$H_j$ = The organic phase molar flow leaving stage J

$R_j$ = Reflux ratio for stage J

$E_{j,i}$ = Extraction factor for component i on any stage J conditions

$k_{j,i}$ = Physical equilibrium constant for component i on stage J conditions

Table 2

### Matrix used for convergence of Equation 10

$$\begin{bmatrix} \frac{\partial B_1}{\partial RM_1} & \frac{\partial B_1}{\partial RM_1} & \cdots\cdots & \frac{\partial B_1}{\partial RM_n} & \frac{\partial B_1}{\partial \theta_1} & \cdots\cdots & \frac{\partial B_1}{\partial \theta_n} \\ \frac{\partial B_2}{\partial RM_1} & \frac{\partial B_2}{\partial RM_2} & \cdots\cdots & \frac{\partial B_2}{\partial RM_n} & \frac{\partial B_2}{\partial \theta_1} & \cdots\cdots & \frac{\partial B_2}{\partial \theta_n} \\ \cdot & \cdot & \cdots\cdots & \cdot & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdot & \cdots\cdots & \cdot & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdot & \cdots\cdots & \cdot & \cdot & \cdots\cdots & \cdot \\ \frac{\partial B_n}{\partial RM_1} & \frac{\partial B_n}{\partial RM_2} & \cdots\cdots & \frac{\partial B_n}{\partial RM_n} & \frac{\partial B_n}{\partial \theta_1} & \cdots\cdots & \frac{\partial B_n}{\partial \theta_n} \\ \frac{\partial F_1}{\partial RM_1} & \frac{\partial F_1}{\partial RM_2} & \cdots\cdots & \frac{\partial F_1}{\partial RM_n} & \frac{\partial F_1}{\partial \theta_1} & \cdots\cdots & \frac{\partial F_1}{\partial \theta_n} \\ \frac{\partial F_2}{\partial RM_1} & \frac{\partial F_2}{\partial RM_2} & \cdots\cdots & \frac{\partial F_2}{\partial RM_n} & \frac{\partial F_2}{\partial \theta_1} & \cdots\cdots & \frac{\partial F_2}{\partial \theta_n} \\ \cdot & \cdot & \cdots\cdots & \cdot & \cdot & \cdots\cdots & \cdot \\ \frac{\partial F_n}{\partial RM_1} & \frac{\partial F_n}{\partial RM_2} & \cdots\cdots & \frac{\partial F_n}{\partial RM_n} & \frac{\partial F_n}{\partial \theta_1} & \cdots\cdots & \frac{\partial F_n}{\partial \theta_n} \end{bmatrix} \begin{bmatrix} \Delta RM_1 \\ \Delta RM_2 \\ \cdot \\ \cdot \\ \cdot \\ \Delta RM_n \\ \Delta\theta_1 \\ \Delta\theta_2 \\ \cdot \\ \Delta\theta_n \end{bmatrix} \begin{bmatrix} B_1 \\ B_2 \\ \cdot \\ \cdot \\ \cdot \\ B_n \\ F_1 \\ F_2 \\ \cdot \\ F_n \end{bmatrix}$$

Table 3

## Molar composition of example feedstock

| Component | Aqueous molar flow, lb-mol/hr | Organic molar flow, lb-mol/hr | Molar frac., aq. phase | Molar frac., org. phase |
|---|---|---|---|---|
| MEA | 8.2 | 0.0 | 0.0153 | 0.0 |
| Water | 525.7 | 0.0 | 0.9847 | 0.0 |
| MEA sulfide | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.0 | 6.5 | 0.0 | 0.0018 |
| Propylene | 0.0 | 802.7 | 0.0 | 0.2234 |
| Propane | 0.0 | 417.2 | 0.0 | 0.1161 |
| i-butene | 0.0 | 798.4 | 0.0 | 0.2222 |
| i-butane | 0.0 | 508.5 | 0.0 | 0.1415 |
| n-butane | 0.0 | 247.6 | 0.0 | 0.0689 |
| i-pentene | 0.0 | 401.7 | 0.0 | 0.1118 |
| i-pentane | 0.0 | 352.5 | 0.0 | 0.0981 |
| n-pentane | 0.0 | 58.2 | 0.0 | 0.0162 |

Table 4

## Experimental constants for Equation 11

| Component | Constant | | | |
|---|---|---|---|---|
| | A | B | C | D |
| MEA | 0.0 | −1.0 | 3.85 | 9.9193431 |
| Water | 0.0 | −1.0 | 1.60 | 5.7643230 |
| MEA sulfide | 0.0 | −1.0 | 1.31 | 5.7643230 |
| $H_2S$ | 0.0 | −1.0 | 1.61 | 6.7643230 |
| Propylene | 1.0 | 0.01 | 1.5326765 | 3.7643230 |
| Propane | 1.0 | 0.01 | 3.0073873 | 7.0243587 |
| i-butene | 1.0 | 0.01 | 2.0205491 | 4.6476130 |
| i-butane | 1.0 | 0.01 | 2.6496884 | 6.5059646 |
| n-butane | 1.0 | 0.01 | 3.3136403 | 7.9193431 |
| i-pentene | 1.0 | 0.01 | 2.2337305 | 5.3433005 |
| i-pentane | 1.0 | 0.01 | 2.8549135 | 6.7340956 |
| n-pentane | 1.0 | 0.01 | 2.0 | 5.0969100 |

Equations 4 and 5 are used to obtain the following expression:

$$a_{j,i} = E_{j,i} \times h_{j,i} \qquad (6)$$

Substitution of Equation 6 into Equation 2 yields:

$$h_{j-1,i} + E_{j+1,i} \times h_{j+1,i} - h_{j,i}(1 + E_{j,i}) = S_i \times RM_j \qquad (7)$$

The equation system resulting from a tray-by-tray mass balance can be solved by arranging it in a tridiagonal matrix form which may be solved through Thomas's method[2] or through any other suitable method.

Usually, the temperature variations between inlet and outlet of each stream in a contactor-type column do not exceed 5° F., so it can be assumed that the behavior of the contactor is basically isothermal.

Using the previously developed equations, the algorithm for the simulation of a liquid-liquid contactor is developed using the following steps:

1. Obtain system data:

- Molar flow and composition, both aqueous phase (MEA solution) and organic phase (LPG)
- Inlet temperature, both aqueous and organic phase
- Contactor operating pressure
- Aqueous phase molar density
- Number of stages.

2. Determine the average temperature of the aqueous organic phase inlet temperatures, and, together with pressure, evaluate the reaction and the physical equilibrium constants for each component.

3. Determine the initial reflux ratio as the ratio between aqueous phase molar flow and organic phase molar flow entering the contactor. Assume that the reflux ratio has the same value for each stage initially. Now, determine the extraction factor for each component in each stage.

4. Do a mass balance through the tower in order to get the molar flow of each component entering and leaving any stage.

5. Create a new function called $B_j$, to make the reaction function coverage, using the Newton method. The new function is defined as:

$$B_j = X_{j,HS^-} \times (A_j)^2 - K_j \times X_{j,MEA} \times X_{j,H_2S} \times DML \qquad (8)$$

where:

$B_j$ = Reaction function under stage J conditions.

6. Find derivatives of $B_j$ with respect to $RM_j$ in each stage.

This process can be done numerically:

- Increase $RM_j$ in increments of $0.001 \times RM_j$[3]
- Evaluate the mass balance of Step 4
- Evaluate a new reaction function, using Step 5
- Find the derivative of $B_j$ with respect to $RM_j$ as follows:

$$\frac{\partial B_j}{\partial RM_j} = \frac{B_j\,(RM \times 1.001) - B_j(RM)}{0.001 \times RM_j} \qquad (9)$$

- With values obtained, fill up the matrix system shown in Table 1. Solve the matrix system and check for $\Delta RM_j$ converging to 0.

If it does, go to Step 7; if not, make $RM_j = RM_j + \Delta RM_j$ and go to Step 4.

7. Now the simultaneous convergence of the reaction function and the mass balance function must be achieved.

The reaction function continues to be the one exposed in Equation 8. The mass balance convergence function is the one obtained by Sujata's method:[4]

$$F_j = \frac{a_{j,i}}{R_j \times H_j} - \frac{h_{j,i}}{H_j} \qquad (10)$$

where:

$F_j$ = Mass balance convergence function for stage J.

Convergence of Equation 10 may be carried out using the Multi-θ method.[5] If the Newton method is used, values obtained will fill up the matrix system shown in Table 2.

Solve this system and check that $\Delta RM_j$ and $\Delta\theta$ converge to 0. If they do, go to Step 8. If not, make $RM_j = RM_j + \Delta RM_j$ and also make $\theta_j = \theta_j + \Delta\theta$. Make a mass balance using updated values for $RM_j$ and $\theta_j$ and repeat Step 7.

At this point, the contactor column simulation is complete.

**Example.** The following example will illustrate the use of the method. Input data are:

Aqueous phase molar flow entering the contactor = 533.8 lb-mol/hr

Organic phase molar flow entering the contactor = 3,593.3 lb-mol/hr

Aqueous phase inlet temperature = 85° F.

Organic phase inlet temperature = 85° F.

Contactor operating pressure = 265 psia

Aqueous phase molar density = 3.356 lb-mol/cu ft (avg.)

Number of theoretical stages = 2

The molar composition of the feedstock components is shown in Table 3.

The reaction equilibrium constant for $H_2S$-MEA in the aqueous system is the one expressed by Holland[6] according to the Kent-Eisenberg Model.

The following physical equilibrium

Table 5

## Stage 1 mass balance

| Component | Aqueous molar flow, lb-mol/hr | Organic molar flow, lb-mol/hr | Molar frac., aq. phase | Molar frac., org. phase |
|---|---|---|---|---|
| MEA | 1.6 | 0.0 | 0.0030 | 0.0 |
| Water | 518.3 | 7.4 | 0.9833 | 0.0020 |
| MEA sulfide | 6.4 | 0.0 | 0.0122 | 0.0 |
| $H_2S$ | 0.0 | 0.0 | 0.0001 | 0.0 |
| Propylene | 0.2 | 802.5 | 0.0003 | 0.2233 |
| Propane | 0.1 | 417.1 | 0.0002 | 0.1161 |
| i-butene | 0.2 | 798.2 | 0.0003 | 0.2221 |
| i-butane | 0.1 | 508.4 | 0.0002 | 0.1415 |
| n-butane | 0.1 | 247.5 | 0.0001 | 0.0689 |
| i-pentene | 0.1 | 401.6 | 0.0002 | 0.1118 |
| i-pentane | 0.1 | 352.4 | 0.0001 | 0.0981 |
| n-pentane | 0.0 | 58.2 | 0.0 | 0.0162 |

Organic phase molar flow leaving the stage = 3,594.3 lb-mol/hr
Aqueous phase molar flow leaving the stage = 527.1 lb-mol/hr
Operating temperature = 85° F.
Operating pressure = 265 psig

Table 6

## Mass balance for Stage 2

| Component | Aqueous molar flow, lb-mol/hr | Organic molar flow, lb-mol/hr | Molar frac., aq. phase | Molar frac., org. phase |
|---|---|---|---|---|
| MEA | 8.0 | 0.2 | 0.0150 | 0.0 |
| Water | 525.7 | 0.0 | 0.9835 | 0.0 |
| MEA sulfide | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.0 | 0.0 | 0.0 | 0.0 |
| Propylene | 0.2 | 802.5 | 0.0003 | 0.2233 |
| Propane | 0.1 | 417.1 | 0.0002 | 0.1161 |
| i-butene | 0.2 | 798.2 | 0.0003 | 0.2221 |
| i-butane | 0.1 | 508.4 | 0.0002 | 0.1415 |
| n-butane | 0.1 | 247.5 | 0.0001 | 0.0689 |
| i-pentene | 0.1 | 401.6 | 0.0002 | 0.1118 |
| i-pentane | 0.1 | 352.4 | 0.0001 | 0.0981 |
| n-pentane | 0.0 | 58.2 | 0.0 | 0.0162 |

Amount of hydrogen sulfide entering the column = 1,108.0 ppm
Amount of hydrogen sulfide leaving the column = 0.0031 ppm
Organic phase molar flow leaving the stage = 3,593.7 lb-mol/hr
Aqueous phase molar flow leaving the stage = 534.5 lb-mol/hr
Operating temperature = 85° F.
Operating pressure = 265 psi

data were experimentally obtained, and are based on solubility data for hydrocarbon-MEA-water system:[7]

$$k = (A - B \times 10^{(C \times \mathrm{Log}(T) - D)})/E \qquad (11)$$

where:

P = Operating pressure, atm
T = Temperature, °F.

A,B,C, and D are experimental constants given in Table 4.

For all components, except $H_2S$, the constant E is defined as:

$$E = 10^{[-3 \times \exp(-6.0598 \times 10^{-4} \times T)]} \qquad (12)$$

For $H_2S$, the constant E is defined as follows:

$$E = P \times 10^{(-0.0055746 \times T - 2.3198952)} \qquad (13)$$

Initial values for $R_j$ and $RM_j$ in each stage were computed, and are $R_j$ = 0.15 and $RM_j$ = 0.001 lb-mol/hr.

Tables 5 and 6 show the mass balance results for each theoretical stage. Stages are counted up from the bottom to the top of the column.

Mass balance results for each theoretical stage were obtained by using a Fortran IV level H program, utilizing the algorithm presented.

This program was run on a Burroughs B-6700 computer, taking 4 sec processing time.

As it can be noted, almost all hydrogen sulfide is absorbed from the LPG stream in the first stage. Although Table 6 does not show any value for hyrogen sulfide contained in the output stream of Stage 1, it is not true totally, since the subroutine for printing the program output was programmed to avoid printing relatively small values.

Still, in the example, the amount of hydrogen sulfide which leaves the extractor column in the sweet LPG stream is shown.

Data related to the feedstock were taken from a gas sweetening unit in a local refinery. Comparisons between the program output and field data showed deviations less than 5% in the worst case.

This shows that the alternate calculation for liquid-liquid extraction column operation involving a chemical reaction is valid.

It is worthy to note that the algorithm proposed can be used for other chemical systems, whenever chemical reaction and physical equilibrium constants are available.

### The author...

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# Processing key to natural-gasoline values

The traditional motor fuels market for natural gasoline, $C_5+$ liquids extracted from natural gas streams, will continue to be the primary market in the future. But Environmental Protection Agency lead phasedown rules reducing lead to 0.1 g/gal, will require further processing of natural gasoline to maintain its value, according to a paper by Dewey Mark of Diamond Shamrock Corp., for the Houston Regional meeting of the Gas Processors Association, Nov. 7, 1985.

Table 1

## Further processing increased natural gasoline value

| | Value ¢/gal | Percent of unleaded price† |
|---|---|---|
| Pre-lead phasedown value: Motor fuel with 1.1 g/gal lead | 73.6* | 86.6 |
| **Post lead phasedown values** | | |
| Natural gasoline | 66.0 | 78.0 |
| Recycle isomerization | 73.7 | 86.8 |
| Reforming | 71.3 | 83.9 |
| Ethylene feedstock | 61.9 | 72.9 |
| Toluene blending | 54.5 | 64.1 |
| Fuel value at $2.00/MMBTU | 22.0 | 25.9 |

* Based on 83¢/gal leaded regular, 89 (R + M)/2
† Based on 85¢/gal unleaded, 87(R + M)/2

Before lead phasedown, natural gasoline was blended directly into the gasoline pool because of its good octane response to lead addition. The paraffinic nature of natural gasoline allowed an octane increase of about 10 numbers with the addition of 1 g/gal of lead, over a base level of about 72.7(R + M)/2.

To illustrate the impact of lead phasedown on natural gasoline values, two processing routes, and optional uses of natural gasoline were investigated by Mark.

**Process routes.** Both recycle isomerization and reforming were investigated as possible processing routes to upgrading natural gasoline.

Isomerization will increase the octane number of natural gasoline by about 15 numbers for a recycle operation (from 72.7 to 88.2), said Mark.

The economics of this upgrade are based on a 10,000 b/d facility, a $23.7 million capital cost, and a 4-year payout requirement. Also, since vapor pressure increases, a debit was included for the amount of butane that must be backed out to meet finished gasoline specifications.

Natural gasoline is considered to be worth 66¢/gal (or 78% of the unleaded price) in the gasoline pool when lead cannot be used compared to isomerate valued at 81.6¢/gal. Operating expenses were estimated at 4¢/gal and capital charges were estimated at 3.9¢/gal.

Based on the above economics, when capital charges are included, recycle isomerization increased the value of natural gasoline 7.7¢/gal, or makes it worth 73.7¢/gal—about 86.8% of the value of unleaded gasoline (85¢/gal).

**Reforming.** Catalytic reforming can be used to upgrade natural gasoline if the natural gasoline is fractionated to obtain light & heavy components. The lighter product (79.4% of the full-boiling-range material) is not reformed but it has a higher octane number, 77.6 (R + M)/2.

The heavier product, 20.6% of the full-boiling natural gsoline, can be upgraded to an 87 octane reformate, said Mark. And the reformate has the additional quality of low vapor pressure.

The economics of the reforming route are based on a 10,000 b/d facility, and a 4 year payout.

The light natural gasoline component is blended directly to the finished gasoline with debit included for both octane and volitility. The heavy component contributes no octane credit or debits, and volitility is credited due to the low vapor pressure of the reformate.

The economics result in a product value for the light component of 73.1¢/gal and a value for the reformate of 64.5¢/gal. Combined, the two components result in a natural gasoline value of 71.3¢/gal, 83.9% of the unleaded value.

**Other uses.** Two possible uses for natural gasoline are as ethylene plant feedstock and as a burner or boiler fuel. Although heavier feedstocks for ethylene production result in less ethylene and more byproduct production, the combined values of ethylene and byproducts can make natural gasoline a suitable feed for ethylene production. Typical ethylene production and byproduct yields for natural gasoline feed are: ethylene, 37.9%; propylene, 14.8%; butadiene, 4.3%; and aromatics, 11.1%.

Based on feeding 10,000 b/d of natural gasoline to an ethylene plant, and based on the values for the byproducts produced, natural gasoline has a value of 61.9¢/gal on a cash operating basis, or 72.9% of the value of unleaded, according to Mark's analysis.

Use of natural gasoline as a boiler or burner fuel is not very attractive, said Mark. The heating value of the combined natural gasoline components is about 110,000 BTU/gal. Based on fuel gas priced in the range of $2.00/MMBTU, the value of natural gasoline would be only about 22¢/gal or 25.9% of the value of unleaded.

The use of natural gasoline with octane enhancers such as oxygenates and toluene was covered by Mark. Toluene was chosen for examination because of its wide acceptance as a high-octane blending agent.

A blend of 53% natural gasoline, 43% toluene, and 4% butane is required to meet gasoline specifications, said Mark. Because of the high price for toluene, the natural gasoline value for this route is only 54¢/gal or 64% of the unleaded value.

The table summarizes the various processing and use routes to utilize natural gasoline as a result of lead phasedown.

From the analyses, Mark concludes that the value of natural gasoline, over the short term, without further processing will drop about 7 to 10¢/gal below pre-lead phasedown levels. But it appears that there is incentive to provide capital expenditures required to upgrade natural gasoline into the motor fuel market. Mark anticipates that economics will dictate that the processed natural gasoline value will be from 2 to 5¢/gal below the pre-lead phasedown levels over the long term.▪